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Proceedings at the Meetings, and Report of the President and Council for the Session 1900–01.

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VII. Illustrative of Prof. J. A. Fleming and Mr. A. W. Ashton's Paper on a Model which Imitates the Behaviour of Dielectrics.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

OCTOBER 1899.

I. *The Magnetic Properties of Alloys of Iron and Aluminium.*—PART I.

By S. W. RICHARDSON, *D.Sc., late* 1851 *Exhibition Research Scholar; Lecturer and Demonstrator in Physics at the University College, Nottingham**.

CONTENTS.

§ I. The Introduction.
§ II. A discussion of the method used for the magnetic measurements, and a description of the apparatus.
§ III. An account of the method used for determining the temperature.
§ IV. An account of the methods used for varying the temperature.
§ V. The data obtained, and some remarks upon them.

§ I. THE INTRODUCTION.

THE experiments made by Hopkinson† on alloys of iron and nickel led to such striking results that the author thought that experiments of the same nature on other alloys of iron might contribute some interesting facts to our knowledge of Magnetism. Accordingly a series of experiments were undertaken on some alloys of iron and aluminium. An account of the earlier experiments on these alloys, performed at the Cavendish Laboratory during the years 1897 and 1898, is given in this paper; the later experiments being reserved for a subsequent communication.

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* Read October 27, 1899.

† 'Proceedings of the Royal Society,' December 1889, January and May 1890.

The alloys were made to the author's order by the British Aluminium Company. Considerable difficulty was experienced at first in obtaining satisfactory specimens, the ones first made being very brittle and liable to split when smartly struck. This was no doubt due mainly to rapid cooling. After taking suitable precautions against this, however, sufficiently durable specimens were obtained—unless the amount of aluminium approached 30 per cent., in which case the alloys gradually disintegrated to fine powder with the evolution of acetylene gas.

The specimens actually investigated contained 3·64, 5·44, 9·89, and 18·47 per cent. of aluminium respectively. The first was comparatively soft and could easily be turned in a lathe; but the other three (in which the carbon was in the combined form) were extremely hard, and it was found impossible to cut them with ordinary tools. The rings used in the experiments were obtained by casting the metal into a disk and boring out the central part of this by means of a rotating copper tube fed with emery-powder and oil.

The experiments made extend over temperatures ranging from −83° C. to +900° C.

To obtain the low temperatures, the specimen, wound with primary and secondary coils, was immersed in an ether bath surrounded by a cooling medium of either ice and salt or carbon-dioxide snow. The ether bath was connected with a water-pump, by means of which rapid evaporation could be set up, and the ether thus cooled below the temperature of the surrounding medium.

The carbon-dioxide snow was obtained from Guinness's brewery, Dublin, and was sent over in a barrel packed with cowhair. Although the journey took three days, the loss due to evaporation was comparatively small, being not more than one quarter of the whole amount. While working with the carbon-dioxide snow the experiments were continued throughout the night, and on one occasion the author conducted an experiment for 36 consecutive hours.

The high temperatures were obtained by means of Fletcher's improved muffle-furnace, furnished with a governor to regulate the supply of gas to the furnace. In later experiments, however, the alloys have been heated electrically by an arrangement similar to that used by Morris* in his experiments on the magnetic properties of iron. This method has been found to be in every respect superior to the furnace method.

The temperatures were deduced from the resistance of the secondary coil, which was of platinum wire, and was wound next to the ring.

The chief results obtained from the experiments recorded in this paper may be summed up generally as follows :—

(1) The alloys behave magnetically as though they consisted of two distinct media superposed.

(2) The general roundness of the curves and their lack of abruptness near the critical point seem to indicate that the alloys are heterogeneous in structure. A similar lack of abruptness near the critical point will be seen in the curves obtained by Hopkinson for nickel-iron alloys.

(3) The permeability decreases with rise of temperature near the critical point until a minimum value is reached, when further rise of temperature produces very slight diminution, if any, in the permeability.

Morris † has shown that in the case of iron we have a remanent permeability after passing the critical point (which result has since been corroborated by Hopkinson ‡).

(4) The experiments suggest that the maximum value of the permeability for an alloy containing 10 per cent. of aluminium is reached at about −90° C.

(5) An alloy containing 18·47 per cent. of aluminium has a critical point of about 25° C., and gives no indication of temperature hysteresis. This alloy probably has a maximum permeability at a temperature much below −90° C.

§ II. THE MAGNETIC MEASUREMENTS.

Theory of the Method.

The ring of metal X (fig. 1) whose magnetic properties are to be investigated is wound with a primary P_2 and a secondary S_2. The primary is connected in series with a battery B, the primary P_1 of a standard mutual inductance-coil Y, an adjustable resistance R, a reversing-key K, and a Weston's ammeter A.

---

* Phil. Mag. Sept. 1897. † *Loc. cit.*

‡ 'Proceedings of the Royal Society,' 1898.

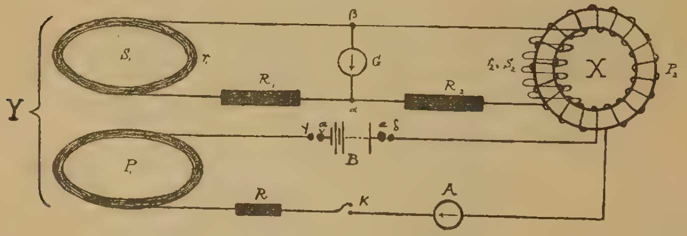
The secondary S_2 is connected in series with the secondary S_1 of the standard mutual inductance-coil Y, and two adjustable noninductive resistances R_1 and R_2.

One terminal of a galvanometer is connected with the point α between R_1 and R_2, and the other terminal with the point β on the opposite side of the bridge.

The secondaries are connected up so that the flows generated in them on reversing the primary are opposed in the branch $\alpha\,\beta$.

The resistances R_1 and R_2 are adjusted until on reversing the primary circuit no *quantity* of electricity passes through the galvanometer.

Fig. 1.



Then, if

B = the induction in the ring X,
σ = the mean sectional area of the ring,
N = the number of turns in the secondary of ring (S_2),
r_2 = the resistance of S_2,
r_1 = ,, ,, of S_1,
M = the mutual inductance of Y,
γ = the value of the steady current in the primary circuit;

we have

$$\frac{B\times\sigma\times N}{R_2+r_2}=\frac{M\gamma}{R_1+r_1},$$

or

$$B=\frac{M}{\sigma\times N}\,\frac{R_2+r_2}{R_1+r_1}\gamma\text{*}.$$

---

* *Cf.* Maxwell, vol. ii. p. 395.

And if

H = the field strength in the ring X,
n = the number of turns in the primary of X,
d = the mean diameter of the ring,

$$H = \frac{4n}{d}\gamma.$$

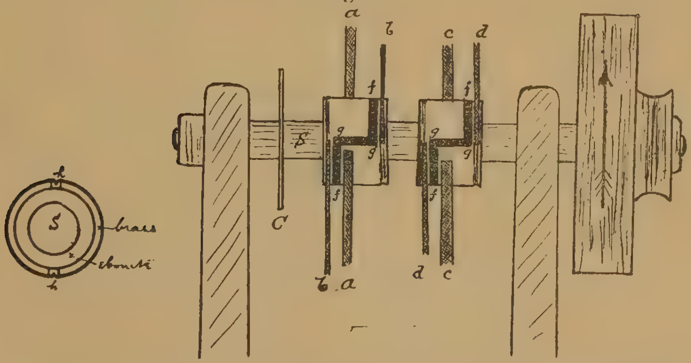
Note.—This is the condition for no quantity through the galvanometer. The condition for no current through the galvanometer cannot be satisfied owing to the variability of the permeability with the field strength. It will, however, be seen later that this did not materially affect the experiments.

Practice of the Method.

The sensitiveness of the method was increased by means of a secohmmeter making about 3 alternations per second.

The secohmmeter D, a diagram of which is shown in fig. 2, consisted of two ebonite rings fitted on to a steel axle S. To each ebonite ring was attached externally a cylindrical brass ring divided along the black lines *f*, *f*.

Fig. 2.

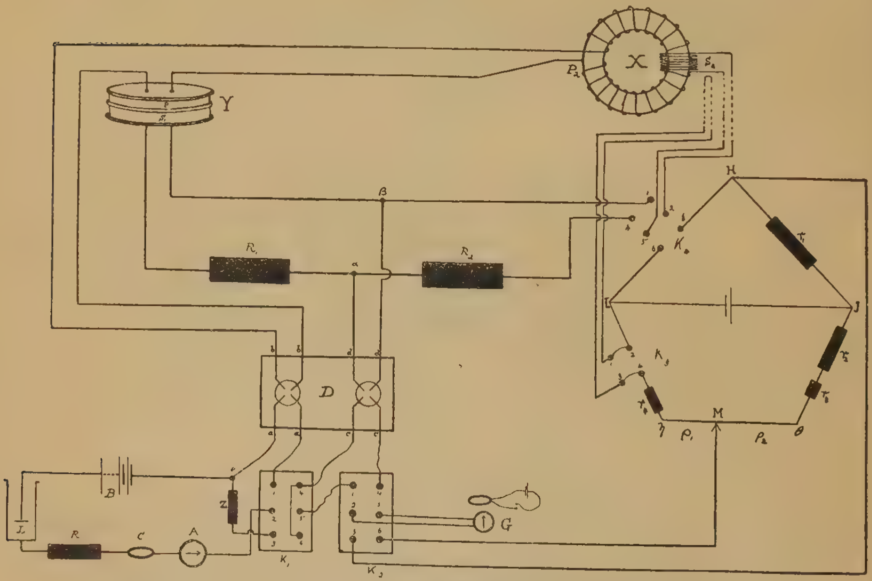


Close to the edges of the brass rings were grooves. In these grooves fitted contacts of copper gauze *b*, *b*, *d*, *d*. Two other pairs of contacts of copper gauze *a*, *a*, *c*, *c*, pressed against the central portions of the brass rings. The contact pieces *a*, *a*, were connected to the two terminals of the battery B, *vide* figs. 1 and 2, and the two terminals *b*, *b*, to the points γ, δ, in the primary circuit (fig. 1). It will be seen that at each half revolution of the secohmmeter the current in the primary circuit was reversed.

The contact pieces *c*, *c* were connected to the two terminals of the galvanometer G (figs. 1 and 3), and *d*, *d* to the points α, β in the secondary circuit. The secohmmeter was driven by a small motor, and the contacts were arranged so that the galvanometer connexions were reversed immediately before the reversal of the battery. The direction of rotation is shown by the arrow (fig. 2).

Pieces of ebonite were fitted into the spaces *g g* to allow the central contacts to pass smoothly over them. In time the insulation becomes impaired owing to the continuous deposition of brass on the ebonite. To prevent this, **V**-shaped grooves *h*, *h* were cut in the ebonite, and thus the continuity of the deposit was broken. These grooves were scraped out from time to time during the experiments.

Fig. 3.



The Branch Circuit.—To prevent the heating of the primary coils due to the passage of the current for any lengthened period a branch circuit Z (fig. 3), whose resistance was equal to that of the primary coils, was made use of.

The brushes *a a* of the secohmmeter D were joined to the mercury cup 1 of the rocker K_1 and to the point *e* respectively. This rocker serves the double purpose of throwing the current in and out of the primaries and of obtaining a zero. This second purpose is considered under a separate heading. The three arms of the rocker on either side are soldered together. In the initial position the points 2 and 3 are connected up, and the current flows through the branch circuit Z. On reversal, the points 1 and 2 are joined, and the current then flows through the primaries of X and Y.

The Galvanometer.—The resistance of the galvanometer finally used in the experiments was about 7 ohms. It was made as sensitive as possible. A weighted needle was used in the first experiments, but was afterwards discarded as it was found that the gain in steadiness was more than outbalanced by the loss of sensitiveness. The needle was never absolutely at rest, owing to the difference of the time constants in the two secondaries, and the variability of that of X. This effect was not sufficient to prevent the detection of a deflexion of $\frac{1}{2}$ millim. on the scale. The scale was read by means of a telescope placed at some distance from the galvanometer. The mutual inductance Y was placed with its axis vertical, and at such a distance from the galvanometer as not to disturb the needle.

To obtain a Zero.—The mercury cups 4 and 6 in the key K_1 are connected. On reversing the rocker, the galvanometer is first cut out and then reconnected. The lengths of the legs of the rocker are such that the current is reversed *before* the galvanometer is reconnected. If the rocker be turned over slowly, the spot of light moves off continuously from the zero.

The Mutual Inductance.—The coil Y was wound with one primary and three secondaries. The values of the mutual inductances for the separate secondaries were $9{\cdot}04 \times 10^6$, $7{\cdot}014 \times 10^5$, and $4{\cdot}536 \times 10^5$ respectively. It was hence possible to vary considerably the value of the mutual inductance used in the experiments. The values given above were determined by comparison with a standard coil whose mutual inductance had been carefully calculated.

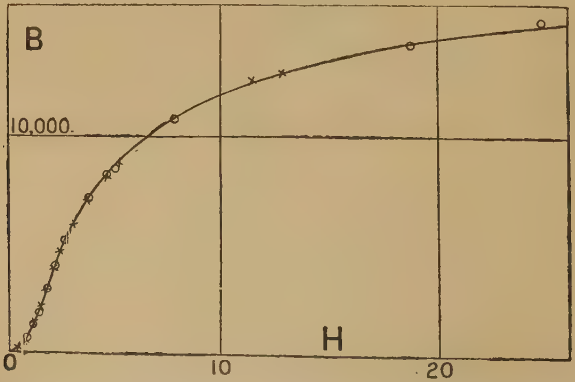
Comparison with the Ballistic Method.—It was thought desirable to compare the results obtained by this method with those obtained from one of the methods in common use. For this purpose a laminated iron ring was wound with primary and secondary coils and was compared with the standard inductance ($=9{\cdot}040\times10^6$), first by the Ballistic Method and secondly by the Balance Method.

The values of the induction obtained in the two sets of experiments are given below.

Ballistic Method.		Balance Method.	
H.	B.	H.	B.
0·97	644	0·52	160
1·24	1,285	0·92	553
1·49	1,870	1·30	1,421
1·85	2,990	1·56	2,190
2·20	4,050	1·81	2,895
2·70	5,230	2·17	3,905
3·90	7,230	2·50	4,730
4·69	8,170	3·13	5,960
5·08	8,470	3·84	7,075
7·82	10,850	4·76	8,150
18·80	14,230	5·40	8,790
24·80	15,150	11·38	12,690
		12·87	13,020
		26·50	15,230

These results are plotted in fig. 4, the ballistic reading being indicated thus ○, and the balance readings thus ×.

Fig. 4.



It will be seen that the two series of results agree with one another within the limits of experimental error.

Eddy Currents.—As the rings used in the experiments were not laminated, the question of the influence of the eddy currents set up in them on reversing the primary became an important one.

In J. J. Thomson's 'Recent Researches,' the case of a cylinder placed in a uniform magnetic field which is suddenly destroyed is considered, and it is shown how the total induction in the cylinder at any time t after the magnetic force is destroyed can be calculated if we know the value of $\frac{4\pi\mu a^2}{\sigma}$, where μ and σ are the permeability and specific resistance of the material of the cylinder and a is its radius. We can make use of this result to form an approximate idea of the speed at which the secohmmeter might be driven without materially affecting the magnetic measurements.

The greatest permeability for alloy No. 1, which is the most permeable of the three specimens considered in this paper, was 680. If we take a as 0·6 cm. and σ as 20,000 (the temperature being 380° C.) $\frac{4\pi\mu a^2}{\sigma}=0{\cdot}15$. A comparison with the table on p. 357 ('Recent Researches') will show that in this case the total induction will have diminished to 1 per cent. of its original amount in 0·1 of a second.

Hence we see that the number of alternations per second in the experiments on this alloy should be less than 10 per second, in order that the results may be relied upon to 1 per cent.

In general the secohmmeter made about 3 alternations per second. It could easily be seen whether, in any given case, the eddy currents were affecting the measurements, by obtaining a balance and then allowing the speed of the secohmmeter to increase.

The effect of eddy currents would be shown by the balance being disturbed.

Care was taken, during the experiments, that the speed of the secohmmeter should in all cases be less than that at which this occurred.

§ III. The Determination of the Temperature.

The resistance of the secondary of the ring (which was of platinum wire and was wound next to the ring) was taken as a measure of the temperature. Thick platinum leads were connected to the secondary close to the ring, and after passing out of the box containing it dipped into mercury cups suspended in an oil-bath. From these cups copper wires passed to the key K_4 (fig. 3), by means of which the secondary could be connected at will to either the magnetic bridge or the wire bridge. Side by side with the platinum leads were placed compensating leads. These were cut from the same specimen of wire as that used for the leads to the secondary, and also dipped into mercury cups suspended in the oil-bath. Copper wires of the same resistance as those connected to K_4 joined these cups with the key K_3.

The object of the oil-bath was to maintain the junctions of platinum and copper at the same temperature, and thus get rid of thermoelectric currents.

The leads were protected from direct heating by the furnace by means of a thick sheet of asbestos.

The resistance-bridge H L M J was so arranged that the resistance of the secondary could be obtained directly from one observation.

This end was gained by the following device:—

The resistance of the arm HJ was made equal to 1001 ohms.

The resistance of MJ consisted of three parts, r_2, r_3, and ρ_2. r_2 was a resistance of 1000 ohms; r_3 consisted of coils of tenths of an ohm; and ρ_2 was part of the bridge-wire $\eta\theta$.

The resistance of the whole wire $\eta\theta$ was slightly greater than 1 ohm. Hence, by taking the proper plugs out of r_3, the resistance of ρ_2 and r_3 could be made together equal to one ohm to within one-twentieth of an ohm; *i. e.*, the resistance of the arm MJ is equal to 1001 ohms to within a twentieth of an ohm. To obtain a reading, the secondary and galvanometer are switched on to the wire-bridge by means of the keys K_4 and K_2, and r_4 and ρ_1 are adjusted until there is a balance [with MJ = HJ].

When this is the case the resistance of the secondary is given by

$$r_t = r_4 + \rho_1.$$

The compensating leads are connected to the arm LM by the key K_3.

The resistance of different lengths of the bridge-wire having been previously tabulated, the resistance of the secondary could be read off directly from the scale.

The temperature t of the ring of alloy was obtained from r_t by means of Callendar and Griffiths's well-known formula

$$t = 100\frac{r_t - r_0}{r_{100} - r_0} + \delta\left[\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right],$$

r_{100}, r_0 being the values of r at 100° C. and 0° C. respectively, and δ having been obtained from observations in the vapour of boiling sulphur.

[To obtain the resistance of the secondary and leads together, the mercury cups 2 and 4 in the key K_3 were joined by a thick copper wire. Then we have, when balance has been obtained as before,

$$r_t + \text{leads} = r_4' + \rho_1'.]$$

As the secondary is outside the ring whose temperature is required, care is necessary to insure that the temperature of the ring does not materially lag behind that of the thermometer.

To avoid the error due to this cause as far as possible, readings were only taken when the temperature was practically stationary.

The close agreement of the results obtained under different conditions shows that the temperature of the ring could not have been greatly different from that of the secondary. As it was impossible to read the magnetic bridge and the resistance bridge simultaneously, the time of each observation was recorded. A time and temperature curve was plotted, and from this the temperature at the time of taking a magnetic observation was inferred.

§ IV. METHODS USED FOR VARYING THE TEMPERATURE AND FOR INSULATING THE COILS.

(1) *Experiments at High Temperatures.*

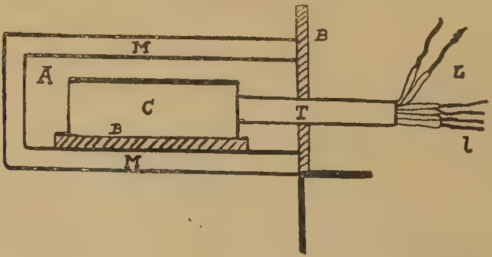
Asbestos paper was used as an insulator in these experiments. The specimen of paper used was obtained from Bell & Sons and was of a very superior quality. After heating to a white heat and subsequently cooling, the discoloration was very slight—the paper then having a faint yellow tinge. The paper also held well together after heating, and showed no signs of crumbling. The amount of carbonaceous matter present must have been very much less than that contained in the paper usually found in the market.

The paper was cut into strips of about 1 cm. width.

A double layer of this paper was wound next to the ring. Outside this the platinum secondary was wound, a double layer of paper being twisted round the wire during winding; this thickness of paper being again doubled for the first and last wind. The primary was of copper wire insulated in the same way as the secondary, a double layer of paper being wound between the primary and secondary.

The ring when wound was placed in a copper box, to which a copper tube of about 8 inches in length was attached.

Fig. 5.



M = muffle.
A = air-space.
C = copper box.
T = copper tube.

B, B = asbestos board.
L = primary leads.
l = secondary and compensating leads.

The box was placed in the muffle of a Fletcher's "Improved Muffle" Furnace, being separated from direct contact with it by means of a thick pad of asbestos board. The mouth of the muffle was closed with another piece of asbestos board, through a hole in which the tube attached to the box passed.

This copper tube, through which the leads passed, served the double purpose of protecting them from the action of the furnace gases and at the same time of maintaining the temperature round them comparatively steady.

The arrangement of the apparatus is shown in fig. 5.

A small governor was connected up between the main gas-supply in the laboratory and the furnace. By this means the pressure of the gas at the furnace was kept constant.

The insulation-resistance between the primary and secondary was tested from time to time during the experiments. It was found to be always greater than 500,000 ohms.

(2) *Experiments at Temperatures between* 0° C. *and* 50° C.

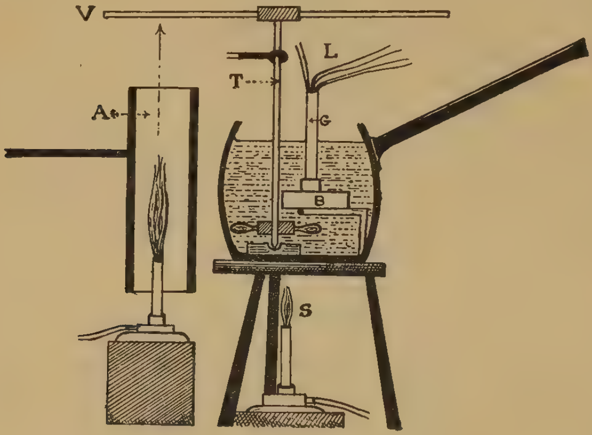
The ring was placed in a thin-walled copper box, which it almost completely filled. A piece of copper tubing of about one inch in length was fastened to one side of the box, and to this was attached a piece of glass tubing of about one foot in length, through which the leads passed. The glass tube was attached to the brass one by means of a joint made with Thomas's alloy. This alloy melts at about 75° C. and expands considerably on solidifying. If a piece of glass tubing is placed concentrically within a brass tube of somewhat greater diameter, and the melted alloy is run into the clear space between the two tubes, a very good mechanical air-tight joint is obtained. A glass tube is used to carry the leads in preference to a metal one, as it is desirable to prevent, as far as possible, the passage of heat between the cavity containing the ring and the external air.

In working at temperatures much below zero this precaution was found very necessary.

The general arrangement of the apparatus is shown in fig. 6. The box containing the ring was placed in a vessel of water which was heated from below by a bunsen-burner. The water was automatically kept in movement by means of a stirrer driven by a current of air passing through an asbestos cylinder and impinging upon a wind-wheel V.

To obtain temperatures between that of the atmosphere and that of ice, the source of heat was removed and small pieces of ice were added to the water from time to time until the desired temperature was obtained.

Fig. 6.



V = wind-wheel.
T = stirrer.
B = copper box.
G = glass tube.

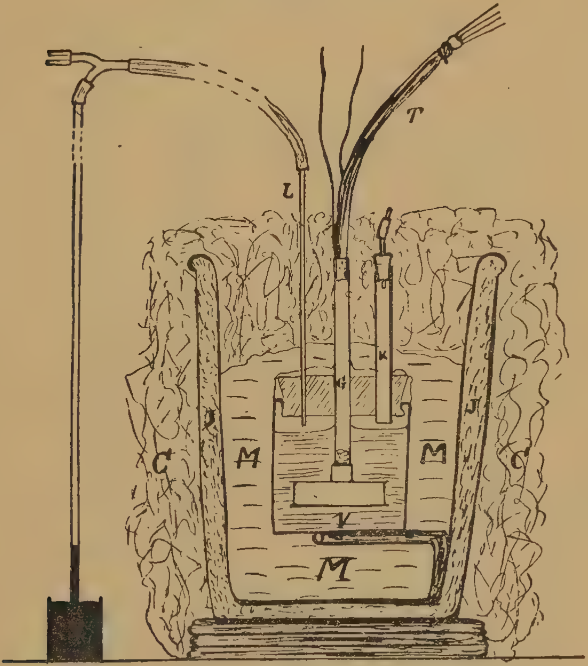
L = leads.
S = source of heat.
A = asbestos cylinder.

(3) *Experiments at Temperatures below Zero.*

The same box and attached tube was used as in the last series of experiments. It was found that, at the low temperatures used, ice formed to the thickness of a centimetre or more along the metal leads, owing to the condensation of the moisture in the air, and thus the insulation was endangered.

To overcome this difficulty the following arrangement was adopted (fig. 7). The secondary and compensating leads were surrounded by an indiarubber tube T, the free end of which was carefully closed. Some portion of this tube passed down into the glass tube G. This was then filled with melted paraffin. By this means the access of moisture to the leads was confined to that in the indiarubber tube, and the formation of ice upon them was almost entirely stopped. The closing of the glass tube also prevented the circulation of air between the surrounding atmosphere and the interior of the box, and the consequent heating of the ring. The box containing the ring was placed in the centre of a thin-walled metal vessel V, which was closed with a tightly-fitting bung through which the glass tube G passed. The vessel V was of about a pint and a half capacity, and was filled with ether, which was introduced through the tube K. The vessel was connected with a water-pump and manometer by means of another tube L. It was thus possible, by the rapid evaporation of the ether, to cool the ring below the temperature of the surrounding medium, and by regulating the evaporation to vary the temperature at will. The bung was covered with melted paraffin before commencing an experiment, to insure air-tightness. The vessel V was placed in the cooling medium M contained in the large stone jar J, which rested on a thick pad of flannel. The whole arrangement was surrounded with a quantity of cotton-waste C. The cooling medium used in these experiments was either a mixture of ice and salt, or carbon-dioxide snow.

Fig. 7.



§ V. THE DATA OBTAINED, AND SOME REMARKS UPON THEM.

Alloy No. I.

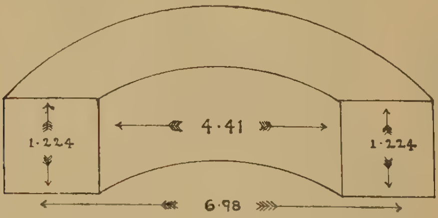
The first alloy investigated contained 3·64 per cent. of aluminium.

This alloy, in which the carbon was mostly in the form of graphite, was comparatively soft, and could easily be turned in a lathe. The other alloys, in which the carbon was mostly in the form of combined carbon, were harder than the hardest steel.

A complete analysis of this alloy, as supplied by Mr. Dawe, is as follows :—

Aluminium	3·64 per cent.
Combined Carbon . .	0·09 „
Graphite	2·40 „
Silicon	2·89 „
Sulphur	0·007 „
Phosphorus	1·086 „
Manganese	0·301 „
Copper	0·112 „
Chromium	traces.
Iron (by difference) . .	89·47 per cent.
	100·00

Dimensions of Ring.



External diameter = 6·98 cms.
Internal „ = 4·41 „
Mean „ = 5·695 „
Thickness = 1·224 „
Mean section = 1·57 sq. cms.

Other data.

Turns in Primary = 87
Turns in Secondary = 61
Mutual Inductance used in these experiments. } = $1{\cdot}155 \times 10^6$.

The following readings of the induction were obtained for different temperatures, the maximum field reached at each reversal being maintained constant during any series of observations.

In the tables

B stands for the induction, in C.G.S. units.
T " " temperature, in degrees centigrade.
H " " field-strength, in C.G.S. units.

Curve (1). H=12·22.

T.	B.	T.	B.
15	3850	435	3130
276	3855	438	3020
315	3855	450	2970
328	3855	476	2885
375	3855	493	2820
386	3855	525	2760
410	3720	540	2690
415	3630	557	2610
428	3240		

Curve (2). H=7·39.

T.	B.	T.	B.
15	2945	415	2730
230	3090	418	2625
268	3215	428	2575
297	3280	437	2550
365	3380	473	2475
392	3335	500	2425
400	3250	510	2390
408	3025	580	2000
412	2780	600	1850

Curve (3). H=4·09.

T.	B.	T.	B.
14	1640	410	2195
147	1735	423	2070
218	1945	425	2055
242	2020	437	2055
297	2275	440	2045
330	2400	450	2030
348	2520	459	2020
372	2600	463	2010
392	2595	467	1995
400	2525	498	1945
		527	1760

Curve (4). H=3·12.

T.	B.	T.	B.
14	1115	397·5	2070
168	1230	410	1790
217	1360	427	1675
242	1460	433	1670
280	1605	440	1660
320	1785	446	1650
342	1945	452	1650
353	2005	462	1645
363	2055	474	1610
380	2115	482	1580
390	2115	525	1405
[397	2110]	579	488

Curve (5). H = 2·20.

T.	B.	T.	B.
14	455	394	1220
195	562	400	1110
253	729	406	1045
283	816	413	997
305	963	415	997
350	1210	420	994
375	1290	424	994
380	1300	431	994
390	1260	460	955
		507	765

Curve (6). H = 1·04.

T.	B.	T.	B.
14	168	397	282
173	185	400	274
260	219	405	265
273	239	408	252
305	253	411	240
328	274	412	231
343	286	417	219
375	295	421	215
387	295	423	202
390	290	467	181
		515	140

Curve (7). H = 0·49.

T.	B.	T.	B.
14	67·7	400	91·0
172	75·9	426	81·5
230	83·3	434	73·1
247	86·3	443	67·2
300	92·7	462	61·0
315	96·0	469	59·1
365	101·0	516	50·8
390	98·6	535	48·2
		544	43·4

Curve (8). H = 1·96.

T.	B.	T.	B.
15	367	585	219
305	736	624	67
345	895	693	18
435	714	785	3·4
457	714	888	3·4
483	681	943	3·4

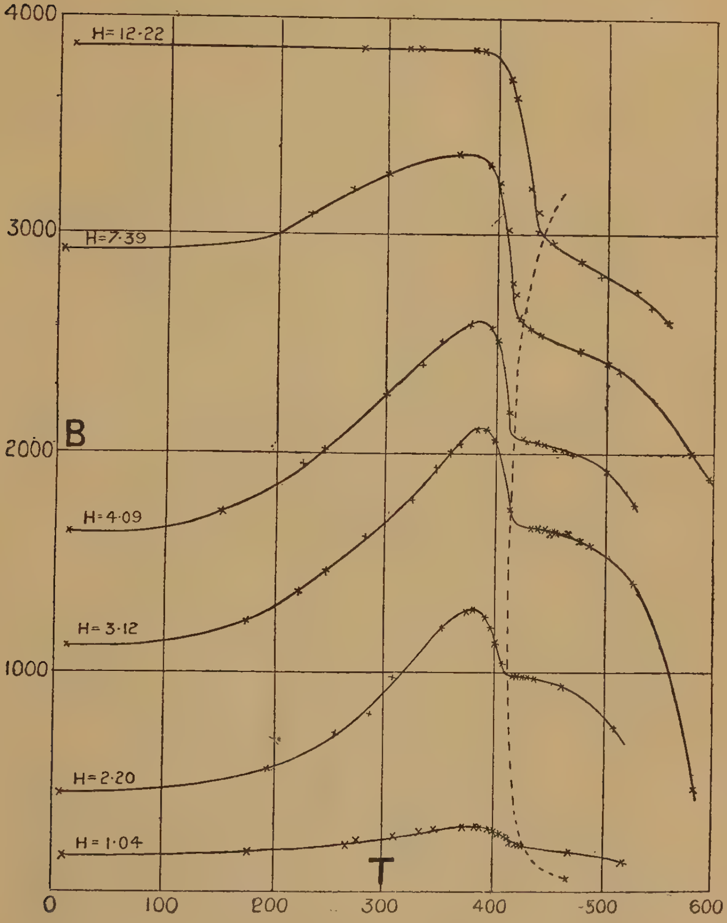
These results are plotted on fig. 8 and on fig. 10. The curves obtained show that the maximum value of the induction is reached at about 380° C. For the next 40° or so the curves are very steep, this steepness indicating a comparatively sudden change in the permeability of the alloy. This steep part of the curve is followed by a very flat part extending over about 100°, for which range of temperature the permeability remains almost constant. This flat part is followed by a steep part extending to about 600°, when the curve begins to bend round again, finally becoming parallel to the axis of temperature at about 750° C.

This temperature was taken as the critical temperature for the ring of alloy.

At about 660° C. the curve develops a sharp point indicating an abrupt increase in the permeability followed by an equally abrupt decrease. This point will be discussed more fully in Part II.

It will be noticed that there are no sharp points in the

Fig. 8.



curves at the temperatures of maximum and minimum permeability as might be expected to be the case if we were dealing with a substance of uniform consistency. This general roundness suggests that the alloy is heterogeneous in structure, the

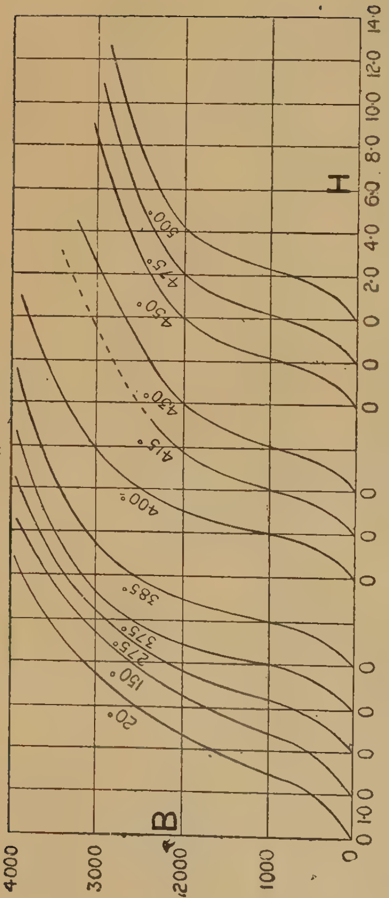


Fig. 9.
B
4000
3000
2000
1000
0
H
0
1·0
2·0
4·0
6·0
8·0
10·0
12·0
14·0
20°
150°
275°
375°
385°
400°
415°
430°
450°
475°
500°

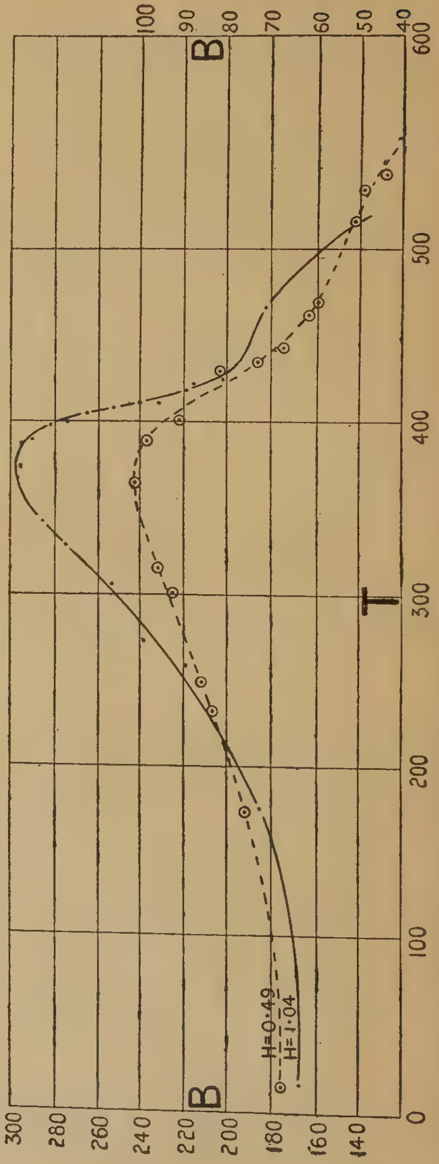


Fig. 10.
B
300
280
260
240
220
200
180
160
140
B
100
90
80
70
60
50
40
T
0
100
200
300
400
500
600
H=0·49
H=1·04

roundness being due to the different constituents reacingh their maximum and minimum values at slightly different temperatures.

Fig. 11.

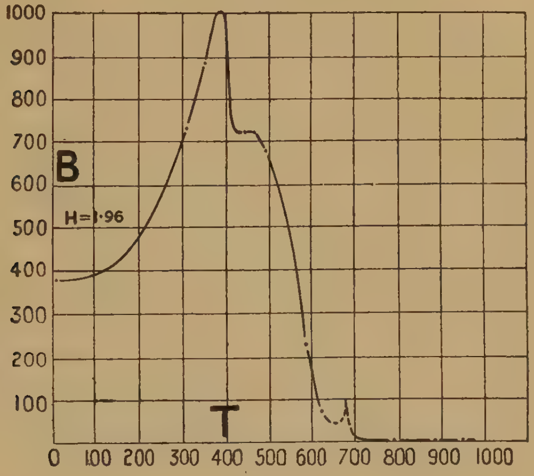
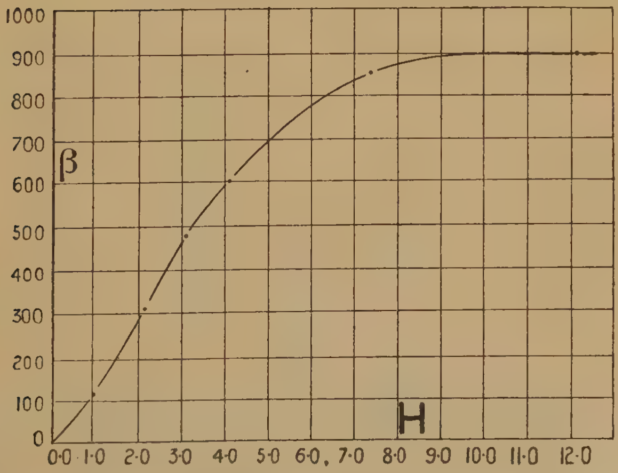


Fig. 12.



A complete curve, showing all the changes of induction with increasing temperature, is shown on fig. 11.

The relatively great steepness of the curve between the temperatures of 385° and 420° (about) is well shown in this figure.

This general form of curve was found to be common to all the alloys experimented on.

In all cases there is a very sudden change in the induction after passing the temperature of maximum induction, followed by a flatness extending in the case of the alloy containing 10 per cent. of aluminium over a considerable range of temperature, after which the curves again become steep.

It was thought that it would be interesting to ascertain whether the magnitude of this sudden change was in any way connected with the strength of the field.

To do this it is easy to select the temperature at which the induction is a maximum, as this is fairly well marked, and is about 380° C. The temperature at which the sudden change ceases does not, however, appear to be the same for all fields. The temperature 450° was arbitrarily chosen as that from which to measure the termination of the sudden change. The difference of B between these two temperatures is for shortness referred to as β.

The following values were obtained for β :—

H.	B at 380°.	B at 450°.	β.
12·22	3860	2960	900
7·39	3375	2520	855
4·09	2630	2030	600
3·12	2130	1650	480
2·20	1300	990	310
1·04	300	187	113

These results are plotted on fig. 12. The curve obtained is very similar in general shape to a B and H curve, and does not differ materially in shape from the analogous curves for the next alloy considered. The changes of the induction with temperature are, in fact, of the same nature as those we

T=20° C.

H.	B.	H.	B.
12·22	3850	3·12	1120
7·39	2940	2·20	470
4·09	1640	1·04	168

T=150° C.

H.	B.	H.	B.
12·22	3850	3·12	1190
7·39	2970	2·20	510
4·09	1740	1·04	178

T=275° C.

H.	B.	H.	B.
12·22	3850	3·12	1580
7·39	3230	2·20	810
4·09	2170	1·04	235

T=375° C.

H.	B.	H.	B.
12·22	3855	3·12	2110
7·39	3380	2·20	1300
4·09	2620	1·04	298

T=385° C.

H.	B.	H.	B.
12·22	3850	3·12	2130
7·39	3360	2·20	1300
4·09	2630	1·04	296

T=400° C.

H.	B.	H.	B.
12·22	3820	3·12	2040
7·39	3250	2·20	1110
4·09	2520	1·04	278

T=415° C.

H.	B.	H.	B.
12·22	(3630)	3·12	1680
7·39	2700	2·20	990
4·09	2080	1·04	225

T=430° C.

H.	B.	H.	B.
12·22	3200	3·12	1670
7·39	2570	2·20	990
4·09	2050	1·04	197

T=450° C.

H.	B.	H.	B.
12·22	2960	3·12	1650
7·39	2530	2·20	980
4·09	2030	1·04	187

T=475° C.

H.	B.	H.	B.
12·22	2870	3·12	1610
7·39	2480	2·20	910
4·09	2000	1·04	176

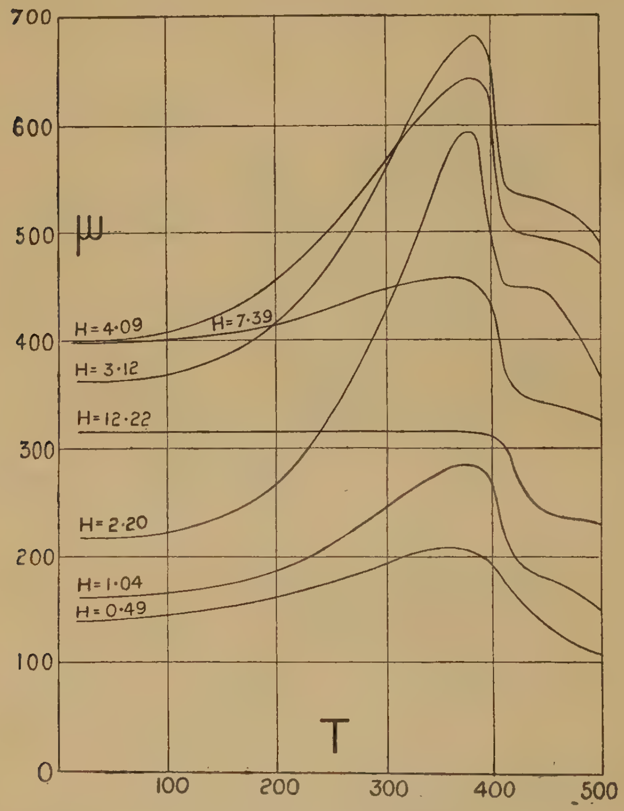
T=500° C.

H.	B.	H.	B.
12·22	2820	3·12	1530
7·39	2420	2·20	810
4·09	1940	1·04	156

should obtain if we were dealing with two rings of different compositions superposed one upon the other.

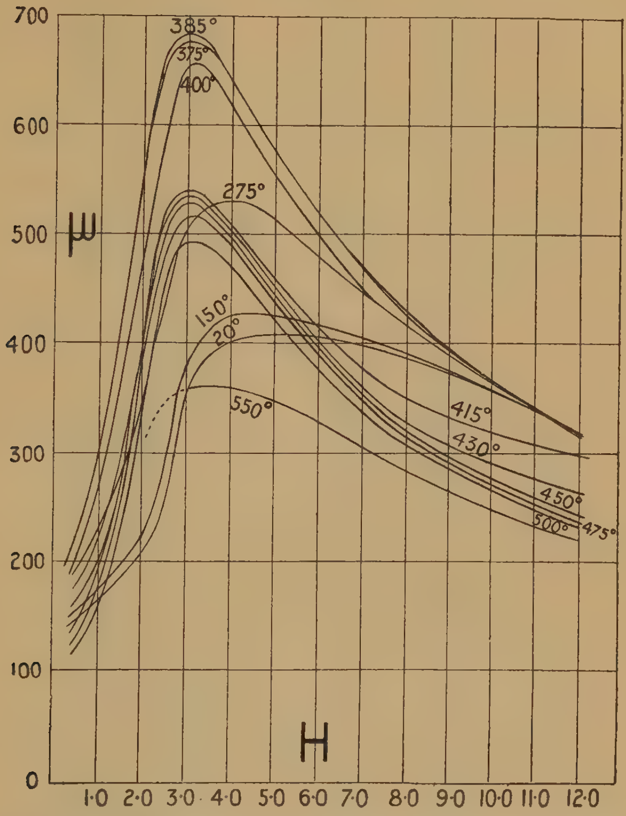
The B and H curves shown on fig. 9 were obtained from the readings given in the Table on p. 23.

Fig. 13.



On figs. 13 & 14 are shown the curves connecting (1) the permeability and temperature when the maximum field reached at each reversal is maintained constant, and (2) the permeability and field-strength when the temperature is constant. The greatest permeability is reached at 380° C. for fields of about 3·0 C.G.S. units, but the increase in permeability between 20° and 380° is greatest for fields of about 2·2 C.G.S. units. The curves are more rounded in general outline both for high and low fields than for fields of medium strength.

Fig. 14.



The values from which these curves were obtained are given on page 26.

Alloy No. II.

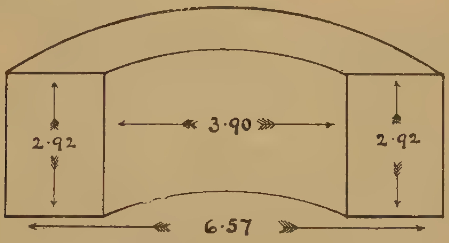
This alloy contained about 10 per cent. of aluminium. It was too hard to be cut by ordinary tools. The molten metal was cast into a ring of 6·57 cms. external diameter, and 2·92 cms. thick. The ring was subsequently cut into two by means of a diamond wheel, and an analysis was made of the upper half.

T.	H.	μ.	T.	H.	μ.
20°	12·22	315	150°	12·22	315
	7·39	398		7·39	402
	4·09	401		4·09	425
	3·12	359		3·12	382
	2·20	214		2·20	232
	1·04	161·5		1·04	171
	0·49	139		0·49	151
275°	12·22	315	375°	12·22	316
	7·39	437		7·39	457
	4·09	530		4·09	640
	3·12	507		3·12	675
	2·20	368		2·20	591
	1·04	226		1·04	286
	0·49	184		0·49	206
385°	12·22	315	400°	12·22	313
	7·39	454		7·39	439
	4·09	643		4·09	616
	3·12	683		3·12	654
	2·20	591		2·20	505
	1·04	285		1·04	267
	0·49	204		0·49	192
415°	12·22	297	430°	12·22	262
	7·39	366		7·39	348
	4·09	508		4·09	501
	3·12	539		3·12	535
	2·20	450		2·20	450
	1·04	216		1·04	189
	0·49	173·5		0·49	155
450°	12·22	242	475°	12·22	235
	7·39	342		7·39	336
	4·09	496		4·09	489
	3·12	529		3·12	516
	2·20	446		2·20	414
	1·04	180		1·04	169
	0·49	135		0·49	118
500°	12·22	231	550°	12·22	217
	7·39	327		7·39	298
	4·09	474		3·12	359
	3·12	491			
	2·20	368			
	1·04	150			
	0·49	110			

Analysis of upper half (by Mr. Dawe).

Aluminium	9·89
Combined Carbon	2·80
Graphite	traces
Silicon	2·75
Sulphur	traces
Phosphorus	0·57
Manganese	trace
Copper	nil
Chromium	nil
Arsenic	nil
Iron (by difference)	83·99
	100·00

Dimensions of Ring.



External diameter	6·57 cms.
Internal ,,	3·90 ,,
Mean ,,	5·23 ,,
Mean thickness	2·92 ,,
Mean section	3·88 sq. cms.

Other data.

Turns in Primary	63
Turns in Secondary	36

Standard Mutual Inductance used$=1{\cdot}155\times10^6$.

The curves connecting B and T (H=const.) for this alloy are shown on figs. 15 and 16.

A study of these curves in conjunction with the corresponding ones for the Alloy No. I leads to the conclusion that the maximum value of the induction is probably reached at a temperature of about −90° C. The great change in the induction between this temperature and +100° C. is very striking, the value at 100° being about one-quarter of that at −90° C., and about one-half of that at 20° C.

Fig. 15.

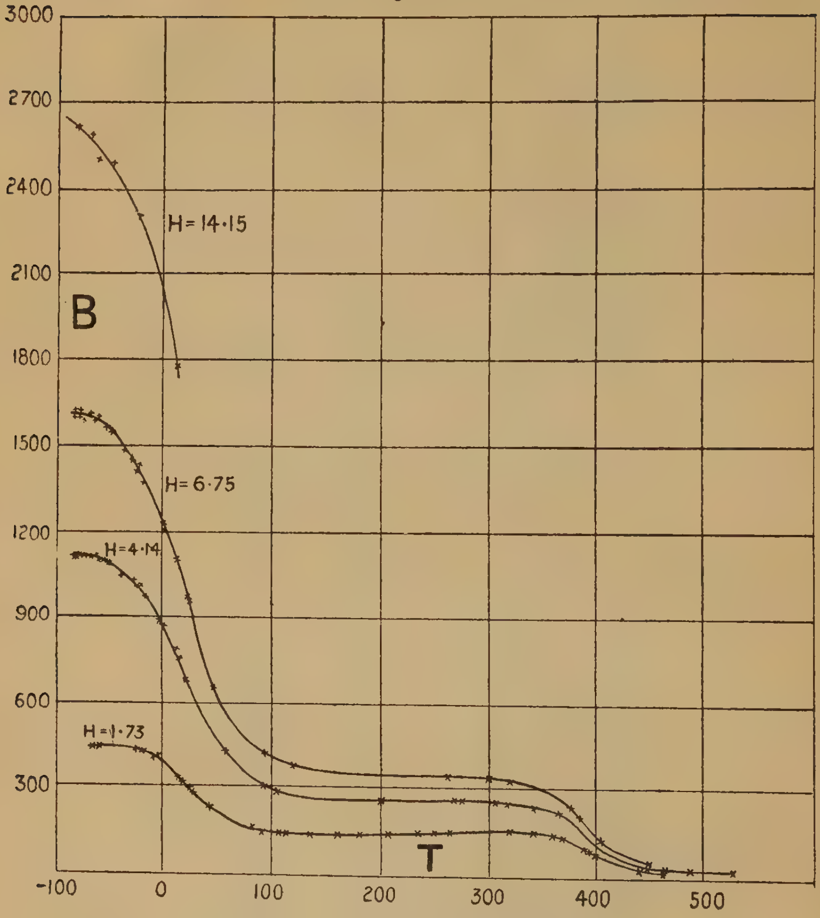
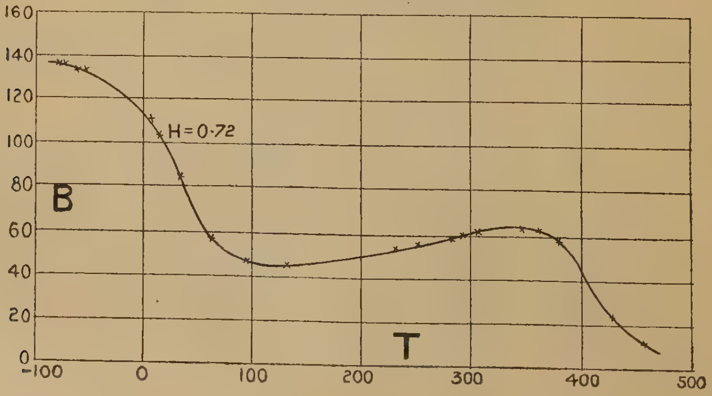

3000
2700
2400
2100
1800
1500
1200
900
600
300
B
H = 14·15
H = 6·75
H = 4·14
H = 1·73
T
-100
0
100
200
300
400
500

Fig. 16.


160
140
120
100
80
60
40
20
0
B
H = 0·72
T
-100
0
100
200
300
400
500

The curves show for weak fields a second maximum between 300° and 400°, after which the induction falls off to a minimum value at about 460° when the permeability = 1·7. All the methods for varying the temperature (*vide* § IV.) were called into requisition in the experiments on this alloy. The method used in obtaining each series of observations is indicated above the series in the tables given below.

Data obtained from Experiments at High Temperatures.

H.	T.	B.	H.	T.	B.
6·75	12	1099	6·75	321	303
	22	951		377	232
	45	641		385	192
	93	404		404	113
	120	359		448	33·4
	263	328		486	12·9
	300	314			
4·14	14	745	4·14	309	238
	57	419		320	232
	90	300		342	219
	104	276		366	206
	200	254		448	24·3
	270	250		461	14·6
	277	245		525	7·0
1·73	13	313	1·73	88	133
	22	282		106	128
	40	223		112	128
	80	148		250	136
	132	125		359	127
	160	126		367	122
	181	127		389	89·5
	207	131		392	74·6
	236	135		398	64·5
	263	136		439	13·5
	320	137		460	5·5
	341	135			
0·72	14	105	0·72	292	59·0
	34	85·5		307	60·4
	62	55·3		343	61·8
	93	45·0		362	61·3
	131	45·2		379	57·7
	230	52·3		427	23·7
	250	55·0		454	10·1
	281	57·7			

Data from Experiments in Ether Bath surrounded by a mixture of ice and salt.

H.	T.	B.	H.	T.	B.
6·75	−2	1242	4·14	−6	880
	−20	1370		−20	966
	−26	1405		−26	1000
1·73	−10	393			
	−20	420			
	−25	425			

Data from Experiments in Ether Bath surrounded with CO_2 snow (First Series).

H.	T.	B.	H.	T.	D.
14·15	−80	2620	14·15	−48	2485
	−68	2590		−22	2260
	−61	2500		+13	1775
6·75	−81	1612	6·75	−61	1587
	−80	1612		−51	1550
	−77	1603		−23	1422
	−68	1600		+11	1103
4·14	−82	1106	4·14	−62	1094
	−80	1106		−53	1082
	−78	1117		−24	1002
	−69	1102		+11	775
1·73	−69	434	1·73	+10	321
0·72	−79	137	0·72	−62	133
	−79	137		−54	133
	−77	137		+9	111

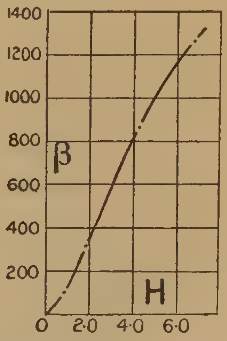
Data obtained from Experiments in Ether Bath surrounded by CO_2 snow (Second Series).

H.	T	B.	H.	T.	B.
6·75	−83	1595	6·75	−38	1477
	−80	1595		−29	1443
	−75	1587		− 1	1207
	−66	1580		+20	960
	−55	1560			
4·14	−80	1110	4·14	−42	1040
	−76	1110		−29	1020
	−67	1105		− 3	860
	−56	1090		+20	673
1·73	−65	434	1·73	− 6	393
				+20	294

β for this alloy represents the difference in the values of the induction at (1) −90° C., and at (2) the temperature of the lowest point reached by the B and T curves between 100° and 200° C. The results are given below, and the curve obtained from them is shown on fig. 17.

H.	β.	
6·75	(1600−340)	1260
4·14	(1110−250)	860
1·73	(435−130)	305
0·72	(138− 44)	94

Fig. 17.



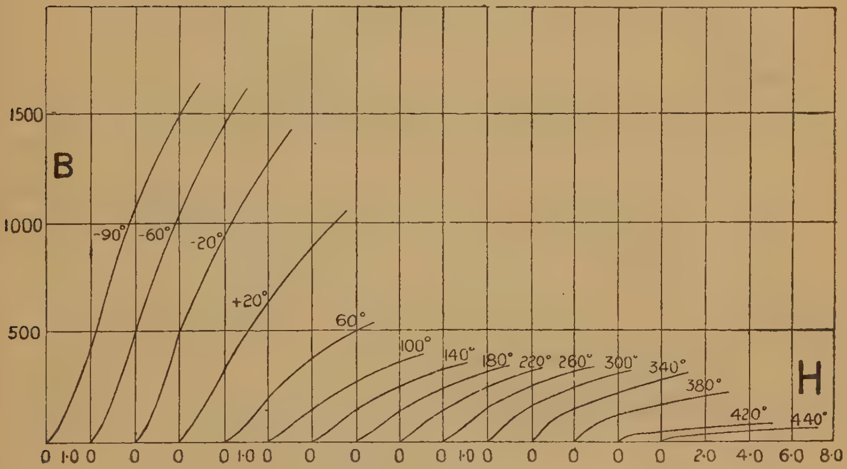
The curve obtained is similar in general form to a B and H curve.

The B and H curves at constant temperature, shown on fig. 18, were obtained from the following readings :—

T = −90° C.		T = −60° C.	
H.	B.	H.	B.
6·75	1605	6·75	1583
4·14	1110	4·14	1095
1·73		1·73	435
0·72	138	0·72	134
T = −20° C.		T = +20° C.	
6·75	1385	6·75	990
4·14	968	4·14	675
1·73	420	1·73	285
0·72	123	0·72	100
T = 60° C.		T = 100° C.	
6·75	533	6·75	390
4·14	400	4·14	280
1·73	175	1·73	130
0·72	57	0·72	45
T = 140° C.		T = 180 °C.	
6·75	350	6·75	338
4·14	255	4·14	248
1·73	125	1·73	125
0·72	45	0·72	47·5
T = 220° C.		T = 260° C.	
6·75	335	6·75	330
4·14	255	4·14	250
1·73	130	1·73	135
0·72	50·5	0·72	55·5
T = 300° C.		T = 340° C.	
6·75	320	6·75	295
4·14	245	4·14	225
1·73	140	1·73	135
0·72	60·5	0·72	63

T=380° C.		T=420° C.		T=440° C.	
H.	B.	H.	B.	H.	B.
6·75	218	6·75	68	6·75	45
4·14	160	4·14	50	4·14	30
1·73	105	1·73	30	1·73	15
0·72	57	0·72	28	0·72	14

Fig. 18.



Alloy No. III.

The third alloy investigated contained 18·47 per cent. of aluminium. It was exceedingly hard. The molten metal was cast into a disk, and a hole was bored through the central part of this by means of the emery cylinder. The critical temperature was found to be about 25° C.

The experiments give no evidence of temperature hysteresis—the B and T curves obtained with rising temperatures being identical with those obtained with falling temperatures.

The great similarity between these curves and the latter part of those for Alloy No. II. (*e.g.* the part above 200° C.) leads to the conclusion that the maximum value of the induction is probably attained at a temperature much below any reached in the experiments.

The curves on fig. 19 (p. 36) show that the values of the induction obtained in the experiments on this alloy can, in the main, be relied on to $\frac{1}{10}$ of a line.

The largest induction observed during the experiments was about 21·5 lines, and the smallest about 2·4 lines.

The greatest permeability was equal to 3·7.

As in the case of the other alloys, there is a remanent permeability after the critical temperature is passed; its value is about 1·5. A curve connecting the temperature and time during cooling did not indicate an evolution of heat on passing the critical point.

As, however, the cooling took place in the air, the test is not sensitive, and this result cannot be regarded as of much value.

The temperature of the alloy during the experiments was regulated by the methods 2 and 3 described in § IV.

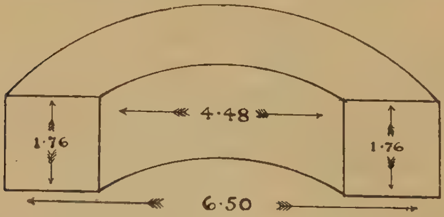
Dimensions of Ring.

External diameter	6·50 cms.
Internal ,, ...	4·48 ,,
,, thickness	1·76 ,,
Mean Section	1·78 sq. cms.

Other data.

Turns in Primary	82
Turns in Secondary	37

Standard Mutual Inductance used $=4·536\times10^5$.



Analysis (by Mr. Dawe).

Aluminium	18·47	per cent.
Combined Carbon . .	1·56	,,
Graphite	0·10	,,
Silicon	1·47	,,
Phosphorus	0·651	,,
Manganese	0·25	,,
Chromium	0·00	,,
Copper	traces	
Iron (by difference) . .	77·50	,,

I.—Experiments with Rising Temperature.

H.	T.	B.	H.	T.	B.
6·11	6	13·1	1·63	7·0	3·6
	8	12·5		8·5	3·4
	20	10·0		19·5	2·7
	37	9·1		37·5	2·5
	51·5	8·6		51·5	2·4
	43 (Temp. falling)	9·0		43 (Temp. falling)	2·4
3·56	6 5	7·6			
	8·5	7·3			
	19·5	5·8			
	37·5	5·4			
	51·5	5·2			
	43 (Temp. falling)	5·4			

II.—Experiments with Falling Temperatures.

H.	T.	B.	H.	T.	B.
6·11	43	9·0	1·63	42	2·4
	26	9·5		26	2·5
	10	11·8		10	3·2
3·56	43	5·4			
	26	5·4			
	10	6·9			

III.—Experiments in Ether Bath, surrounded by CO_2 snow.

H.	T.	B.	H.	T.	B.
6·11	−83	21·0	1·63	−83	5·5
	−80	20 9		−80	5·5
	−78	20·9		−79	5·5
	−74	21·0		−74	5·4
	−63	21·2		−64	5·5
	−50	21·5		−54	5·5
	−31	21·4		−35	5·5
	−14	19 0		−15	5·0
	+ 1	15·2		0	3·9
	21°·1	9·6		21°·1	2·6
3·56	−83	12·1			
	−80	12·0			
	−78	12·1			
	−74	12·0			
	−63	12·2			
	−53	12·4			
	−33	12·3			
	−14	10·9			
	+ 1	8·8			
	21°·1	5·6			

These results are plotted as fig. 19.

Fig. 19.

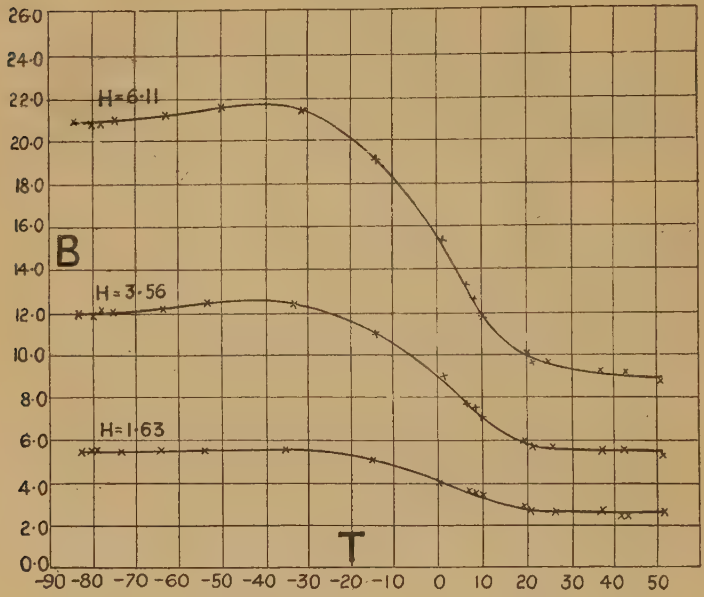
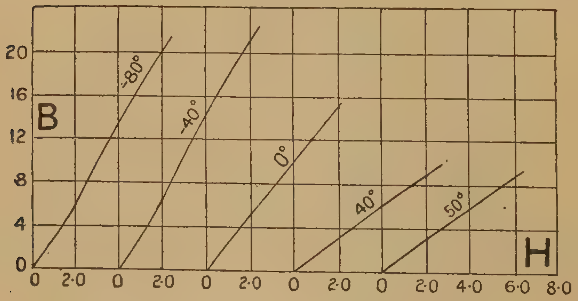


Fig. 20.



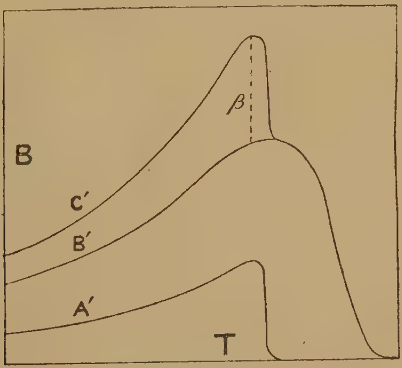
The B and H curves shown as fig. 20 were obtained from the following readings:—

H.	B. T=−80°.	B. T=−40°.	B. T=0°.	B. T=40°.	B. T=50°.
6·11	21·0	21·6	15·5	9·0	8·7
3·56	12·0	12·0	8·8	5·4	5·4
1·63	5·5	5·5	4·0	2·4	2·4

It is not proposed at this stage to enter at length into a consideration of the explanation of the observed phenomena; but it is interesting to notice that the characteristic B and T curve is of the same form as that which would be given by the superposition of two media of different constitution, as for instance crystals in a solidified mother-liquid. That this is so can easily be seen by the consideration of the following diagram.

Suppose, for instance, A′, B′ are the curves obtained by plotting the parts of the induction contributed by each medium independently against the temperature for any given value of H; then the curve C′ obtained by adding the ordinates will represent the observed B and T curve for the alloy in question.

Fig. 21.



The value of β for this curve, which approximates to the maximum value of the ordinate of the curve A′, would then be connected with H by a curve similar to a B and H curve.

This result is in agreement with the curves actually obtained from the experiments.

It is intended very shortly to publish an account of some further experiments on the changes of hysteresis as the temperature rises, and on the behaviour of the alloys during cooling.

In conclusion, the author's best thanks are due to Mr. Dawe, F.I.C., Chemist to the Ebbw Vale Ironworks, for his kindness in making the very complete analyses of the alloys, and to Prof. J. J. Thomson for suggestions and encouragement during the progress of the work.

University College, Nottingham.

Discussion.

Prof. Barrett communicated a note "On the Electric and Magnetic Properties of Aluminium and other Steels." The first part of the note dealt with the electrical conductivity of various alloys, and discussed the effect of composition and annealing upon the value of the conductivity. The second part of the note referred to magnetic effects. The most remarkable effect produced by a certain percentage of aluminium on iron is the reduction of the hysteresis loss. The permeability of nickel steels is shown to be very much influenced by annealing. It is found that the addition of a small quantity of tungsten to iron hardly affects the maximum induction, yet increases the retentivity and coercive force. The experiments show that the best steel for making permanent magnets is one containing 7½ per cent. of tungsten.*

Prof. S. P. Thompson drew attention to the wide range of temperature over which the author had conducted his experiments, and also to the small number of alloys used. He said a very much finer connection between the properties could be obtained from the examination of more alloys, and expressed his interest in the existence of the second maximum on the induction curve. He would like to know how the percentage composition of the alloys had been determined. Turning to Prof. Barrett's note, Prof. Thompson referred to the difference in the breadths of the hysteresis curves for aluminium and chromium alloys.

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* See Trans. R. Dubl. Soc. vii. pt. iv.

Mr. **Appleyard** asked for information upon the permanence of the curves.

Dr. **Richardson**, in replying, said that the specimens were cast in the form of disks—the central portions of which were subsequently bored out and used for the analyses. He also said that Prof. Arnold of Sheffield was endeavouring to obtain a series of very pure specimens for him, which he proposed to investigate with a view to finding out what effect, if any, the impurities produced on the phenomena.

II. *Contact Electricity.*

By **Frederick S. Spiers**, *B.Sc.*, *A.C.G.I.*[*]

§ 1. The object of this investigation was to determine, in a more satisfactory manner than has hitherto been attempted, the part that the medium plays in the P.D. that is observed between two dissimilar metals when they are metallically connected. No experiment on this important point, whether made *in vacuo* or in any gas whatsoever, can be considered decisive unless the films of air condensed on the two plates of metal be first removed. If the Volta effect is due to the air at all, it is most certainly due to that part of the atmosphere immediately surrounding the metals, namely, to the condensed surface-layers of air or oxygen; and hence it is in the highest degree essential to be certain of the entire removal of this surface-layer before any experiments can be considered decisive. The molecular attraction between a metal and the gaseous film in close contact with it is probably of very considerable magnitude; hence it is useless simply to surround the metals with another gas, and then assume that your measurements are being made in that second gas, ignoring the original condensed sheet of air.

Most experimenters on the subject have either ignored altogether or else failed to realize in full the presence and possible action of these air-sheets condensed on the metals. A critical and, I may add, wholly delightful account of the work done prior to the year 1884 is to be found in the exhaustive report presented by Prof. Oliver Lodge to the British Association in that year. Nobody will venture to claim finality for any experiment bearing on the subject that is described in that report. Neither can it be said that any work published since that date effectually and decisively clears up the many doubts and difficulties with which this matter bristles. There are, however, two important researches concerning which a few remarks here would not be out of place. One of these is by Dr. J. T. Bottomley, F.R.S.*, and the other by Dr. J. Erskine-Murray, F.R.S.E.† Dr. Bottomley merely measured the Volta contact-difference between two disks of zinc and copper in high vacua of air and hydrogen, the pressure being less than $\frac{1}{523}$ mm. of mercury, and showed that on readmitting air to atmospheric pressure no variation of the P.D. as great as 1 per cent. ensued. Seeing that Dr. Bottomley did not so much as warm his vacuum-tube, there is not much reason to suppose that the result would have been otherwise than what it actually was. Dr. Erskine-Murray, who quite realized the possible importance of the condensed air-films in the production of the Volta phenomena, attacked the problem rather more indirectly; but his method of removing the films by filing the surfaces of the metals under melted paraffin-wax cannot, I think, be considered as entirely satisfactory. In the first place it ignores the probable electrolytic action of the wax, or of the moisture in the wax, for apparently no precautions were taken to dry it; and even if these effects be disregarded, I believe it improbable in the highest degree that merely filing off the surface-layer of metal is sufficient to remove these condensed air-sheets. Why, the file itself is covered with a film of air!

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[*] Read November 10, 1899. (Communicated by Prof. Ayrton.)

§ 2. It seemed, therefore, that in spite of the enormous quantity of experimental work that this controversy concerning the contact effect had brought forth, there was still room for a crucial and decisive experiment which should go to the very root of the matter, and finally satisfy all conflicting parties. It was with this ideal, possibly unattainable like all true ideals, in view, that I began experiments in this field some two years ago.

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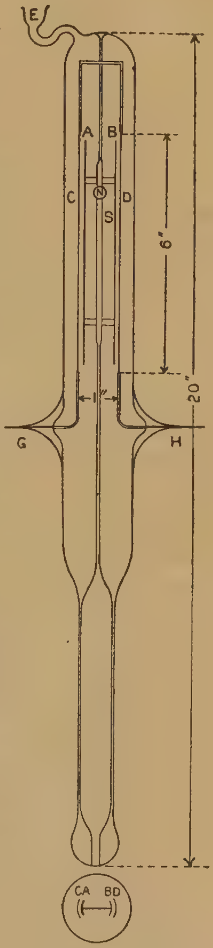
* B. A. Report, 1885.

† Proc. Roy. Soc. 1898, vol. lxiii. p. 113.

§ 3. I will now proceed to describe in detail the various forms of apparatus that were devised for these investigations, and give a short account of the experiments that were made with each. As a rule, only the outlines and results of each experiment will be given; consequently but a small proportion of all the observations taken will be recorded here.

Fig. 1.



§ 4. Some preliminary experiments were made with the apparatus sketched in fig. 1, which was made for Profs. Ayrton and Perry about twenty years ago. In this they adopted the same principle as that used by them in the exhaustive series of contact E.M.F. measurements they made in Japan*. In the figure A and B represent the contact-couple, in this case zinc and platinum. They are metallically connected through the brass spindle S, with which they can revolve, there being a small magnet, N, fixed in the spindle which can be pulled round by an external horseshoe-magnet revolving on a turntable. C and D are two inductors of platinum rigidly fixed, top and bottom, in glass supports. In consequence of the Volta force, A and B are at different potentials, real or apparent. If now C and D be connected to the respective terminals of a quadrant-electrometer, brought to the same potential, and then one of them insulated and A–B turned through 180°, there will be a P.D. induced between C and D which, *cæteris paribus*, is proportional to the contact P.D. between A and B. (See Ayrton and Perry's papers quoted above.) The tube could be connected to a sprengel-pump by means of an indiarubber covered joint in the cup E, sealed in mercury.

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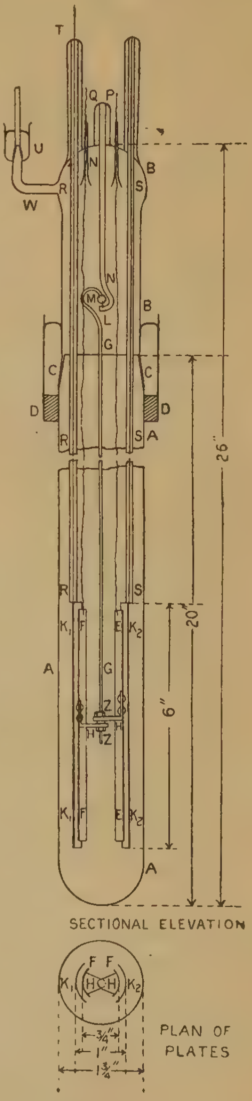
[*] See Proc. Roy. Soc. 1877 & 1878; Phil. Trans. 1880.

The results obtained were not very satisfactory. The apparatus had been lying about in dusty cupboards for many years with the opening unclosed, so that the insulating-power of the glass supports was anything but high. In consequence of the small capacity of the system, quite a small amount of leakage caused a large change in the potential of the insulated inductor; and it is quite possible that the paraffin-wax in which the terminals G, H were sealed was not a sufficiently good insulator for this purpose. It was not possible to measure the absolute value of the Volta P.D. between A and B, as the two metals were in permanent metallic contact inside the tube; one could only measure any relative changes that took place in that value.

Fig. 2.



Several readings were taken in very high vacua, from about $\frac{1}{5000}$ mm. of mercury pressure and upwards (as measured on a McLeod gauge), and a decrease of about 2 or 3 per cent. was observed in the deflexion when the tube was exhausted, the original value returning in each case when air was readmitted into the apparatus. In consequence of the vagueness of the readings, however, not much stress must be laid on these results.

§ 5. In designing a new apparatus, the following points were specially kept in view:—(1) The desirability of being able to measure the actual value of the Volta effect. (2) The absolute necessity of being able to heat strongly the contact couple in the highest attainable vacuum. (3) The necessity of having high insulation in consequence of the small capacities dealt with. It will be found subsequently that the exigencies of (2) reduced the capacity still further than would otherwise have been the case.

To fulfil condition (2) it was necessary to make the apparatus of hard combustion-tubing; but as such glass is extremely difficult to work, and as it would have been exceedingly troublesome, if not impossible, to seal glass tubes or platinum wires into it, it was decided to make the apparatus in two parts. This had the further advantage that the plates could be taken out and examined whenever desirable, which would not have been the case had the tube been entirely sealed up.

The apparatus is shown in fig. 2. A, A the lower half of the tube is made of the hardest combustion-tubing $1\frac{3}{4}$ in. in diameter. It fits into the upper portion B, B, made of softer tubing, at the very carefully-ground glass joint C. The joint is sealed in mercury contained in a glass vessel, which slips over the rubber ring D. The two dissimilar metals E and F form the contact couple. Their dimensions are $\frac{3}{4}$ in. by $5\frac{3}{4}$ in. They are attached to the aluminium spindle G by means of the zinc lugs H, H, to which they are screwed. The spindle passes through slits in these lugs, and they are kept tightly in place by means of the small nuts Z, Z which screw on to G. The nuts are insulated from the bolts and shaft and from one another with strips of mica. The spindle G is mounted at L on a needle-point that rests in a small hole in the glass support N, which is shaped as shown in the figure. M is the end view of a small bar-magnet which is screwed on the spindle. By means of an outside horseshoe-magnet revolving on a turntable one is able to turn M, and therefore the contact couple, through an arc of 180°, just as in the apparatus described in § 4.

Two very fine platinum wires are connected to the dissimilar metals E and F and pass out of the top of the glass tube through the seals at P and Q *. K_1, K_2 are the platinum inductors (each $\frac{7}{8}$ in. by $5\frac{3}{4}$ in.). These are bent into arcs of circles as shown in the plan of fig. 2, and sealed into the highly insulating glass tubes R & S. Platinum wires running

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* It was an operation of some difficulty, even to the practised glass-blower, to make so many seals into one small piece of glass.

through these tubes pass from the inductors K_1, K_2 to the outside of the apparatus, into which they are sealed. The wire which was always kept earthed is sealed at T, as shown in fig. 2. In the case of the insulated one S, it was necessary to prolong the glass tube as shown in fig. 3 (S, S), so that a couple of inches of its surface could always be kept highly insulating by the common device of slipping on it a small flask containing a little strong sulphuric acid (T, fig. 3). The cork (U) is just slipped upwards when readings are being taken. This flask is not shown in fig. 2, as it would there appear in front of the apparatus instead of at the side, as in fig. 3. The outlet W (fig. 2) served to connect the tube to the air-pump. U is a ground-glass joint sealed in mercury.

§ 6. The method employed of measuring the contact P.D. between E and F was a combination of Ayrton and Perry's method (described in § 4) and the well-known compensation method used by Lord Kelvin *. The plates E and F were connected through the platinum wires ending at P and Q to two points on a potentiometer. The one inductor K_1 was joined to the earthed quadrants of the electrometer, the other K_2 to the insulated quadrants. The variable potentiometer contact was then adjusted until, on insulating K_2 and reversing the contact couple by means of the outside horseshoe-magnet, no deflexion of the electrometer needle took place. When this stage was reached the impressed P.D. from the potentiometer exactly counterbalanced the Volta E.M.F. between the plates E and F. A voltmeter gave the reading directly.

§ 7. The method of heating the lower part of the tube was to slip over it a tube of copper lined with asbestos. It was then found quite possible to bring the tube safely to a bright red heat with a blowpipe flame. The large distance between the source of heat and the upper part of the tube, only about 6 or 8 inches of the lower part being heated directly, prevented the joints and seals from becoming unduly heated, and conveyance of heat by convective air-currents was prevented by suitably placed sheets of asbestos cloth. It was at first feared that a large ground-glass joint such as C, C (fig. 2) would not be sufficiently air-tight for the very high vacua

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* B. A. Report, 1880, and 'Nature,' April 14th, 1881, also Dr. Lodge's Report B. A. 1885.

that it was desired to work with, but the joint proved to have been so very carefully ground * that when scrupulously clean it would readily hold a vacuum as high as $\frac{1}{10,000}$ mm., which was almost the limiting reading reliably given by the McLeod gauge. I always found that I could get a far better fit, although, on the other hand, it was then far more difficult to open after exhaustion, when the joint was quite clean and dry than when it was smeared with even a slight trace of glycerine.

In other respects the apparatus did not prove so satisfactory. In the first place it was necessary that the fine platinum wires attached to the movable plates E and F should be so flexible as not to exercise any appreciable control on the free motion of the system. On the other hand, if they were too loose there was fear of one or other of them coming into contact with the platinum inductors at some position through which it passed. It proved an exceedingly troublesome operation to make the exact adjustment of length necessary, and even at their best the wires always exercised a certain amount of control, so that it was never possible to revolve the moving system completely through 180° of arc. This, of course, materially diminished the sensibility of the arrangement. There was another cause which operated still more in reducing the sensibility, and that was the comparatively large distance between the movable plates and the inductors. This was in consequence of the necessarily great length of the spindle G, G, so that when the plates were closer than about $\frac{3}{16}$ in., quite a small amount of side play caused by pulling round the system was sufficient to bring the plates into contact.

When the apparatus was working at its best, and the various adjustments were made with the utmost possible care, a P.D. between the movable plates E and F of one volt caused a deflexion on the electrometer of about 20 scale-divisions, the sensibility of the electrometer being such that a P.D. of a volt applied directly between its terminals gave a deflexion of 470 scale-divisions.

It was impossible to increase the size of the plate and thus

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* I might mention that the glass-blowing required in all these pieces of apparatus was most satisfactorily performed by Mr. C. E. Müller.

augment the sensibility of the apparatus, because its dimensions were strictly limited by the diameter of the combustion-tubing (A, A, fig. 2). I was fortunate enough to get hold of a length of 1¾ in. diameter. As far as I am aware there was not another piece of combustion-tubing in London of greater, or even as great, diameter.

§ 8. In the first experiments that were made with this apparatus the dissimilar metals were platinum and zinc. The P.D. between the two, after cleaning the latter with emery-paper and wiping with clean dry silk, was about 0·95 volt. To make measurements in high vacua I first exhausted the tube to a vacuum of about $\frac{1}{2000}$ mm. (this took about four hours to obtain), without applying any heat at all. This caused no appreciable reduction of the contact force. (In these experiments the degree of accuracy is not greater than 0·05 of a volt.) The tube was then gently heated with a single bunsen-flame, and the pressure soon rose, by reason of the heat driving off occluded or adherent gases from the glass and metal surfaces, to about $\frac{1}{80}$ mm. Long-continued heating with this single bunsen-burner did not noticeably reduce the P.D. between the metals, so an additional source of heat was applied in the shape of another burner; but after a couple of hours' heating and pumping, although air still continued to come off, no change in the P.D. was observed after the metals were allowed to cool.

The tube was next heated in a blowpipe flame, the outer copper shield being kept at a red heat for about 10 minutes. Copious air-bubbles now passed through the fall tubes of the sprengel-pump, and the pressure fell from $\frac{1}{2000}$ millim. to $\frac{1}{100}$ millim. The apparatus was then allowed to cool, the pump being worked continuously. When it was quite cold the pressure was $\frac{1}{6000}$ millim., and the P.D. had fallen to about 0·1 of a volt. It will be seen from § 10 that this was simply the result of oxidation of the zinc, but at the time I thought it might have possibly been a true diminution of the Volta effect due to my having driven off the greater part of the condensed air from the surface of the metal plates. I therefore again heated the tube in the blowpipe flame, this time more strongly than before. Unfortunately the heat proved too fierce for the zinc plate, for it volatilized, covering nearly the whole of the inside of the apparatus with a fine layer of zinc dust. The tube therefore had to be dismantled and opened, thoroughly cleaned, and a fresh plate of zinc put in place of the old one. I thought it best this time not to use the blowpipe at all, but merely to heat the apparatus with a couple of bunsen-burners, continuing heating and pumping until no more air should come away through the pump. But here again, after about five hours' heating, the zinc again melted and the experiment proved useless. I then decided to dispense with the zinc plate altogether and to replace it by a plate of aluminium, whose melting-point is 600° C., while that of zinc is 412° C.

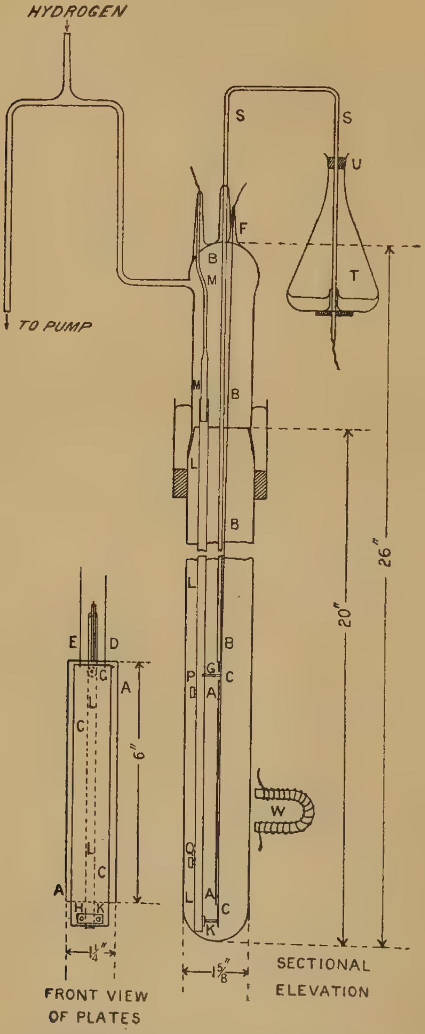
In the course of the next series of experiments I unluckily broke both the upper and lower parts of the tube just at the middle joint C, C in exercising a little too much vigour in separating the two parts from one another after the usual persuasive means of loosening obdurate ground-glass joints had proved unsuccessful. As the apparatus had to be entirely remade I introduced some radical changes in its construction in order to remedy the inherent defects of the original design.

§ 9. Fig. 3 represents the new apparatus as finally constructed. I here adopted the original Volta method of procedure, with the application, of course, of Lord Kelvin's compensation device. In this particular form of apparatus, where great capacity can only be attained by diminishing the distance between the condenser-plates, it is susceptible of greater sensibility than the Ayrton and Perry modification, and it is, moreover, somewhat simpler.

In the fig. A, A is the insulated platinum plate supported and insulated by the glass tube B. To insure rigidity, the plate was fairly stout, too thick to be fused into the glass support, so that it had welded to the top a stout piece of platinum wire which fitted tight into the glass tube B. C, C forms the second plate of the contact couple (at first aluminium and afterwards iron). It is suspended by two very fine platinum wires D and E (front view of plates) that are sealed into the upper part of the apparatus F, so that when C hangs freely, it does so parallel and very close to A, A. The plates are prevented from coming into contact by the three stops G, H, and K. The stop G screws into the aluminium tube

L; H and K into the small cross-piece that is shown in the figure (side view of plates). The tube L fits tightly over the glass rod M that is fused into the head of the tube.

Fig. 3.



A platinum wire which runs down M serves to earth the tube L. The latter tube also serves another purpose, namely, to carry on the small aluminium supports P and Q an electrostatic shield of aluminium that half encompasses the insulated plate A, A. (It is not shown in the figure.) The shield has two slits shaped thus that just slip over the heads of P and Q. It was not necessary to completely shield A, A, as the plate C, C itself, which is of course earthed, serves as a partial shield. In other respects the apparatus is essentially the same as the older one which it replaced.

There is no need to discuss here the well-known method of making an observation. In the actual apparatus (fig. 3), C, when not of iron, had a plate of that metal attached to its back, so that by closing the circuit of the small electromagnet W by means of a spring key it was drawn away from the platinum plate A. This reduced the taking of a reading to the exceedingly simple operations of making and then breaking a single platinum contact to the potentiometer, and then pressing a spring key.

In its new form the apparatus proved entirely satisfactory in every way. The adjustments were not at all troublesome to make, in fact, it was eventually found possible to dispense altogether with the stops L, H, and K (fig. 3), for the plates could be prevented from touching and yet allowed to come within $\frac{1}{15}$ in. of one another by just giving the proper tilt to the apparatus as a whole. The sensibility was all that was desired. When that of the quadrant electrometer for directly applied E.M.Fs. was 553 scale-divisions per volt, a P.D. between the condenser-plates of 1 volt gave on the average a deflexion of about 70 on pulling away the movable plate. It was quite possible, by taking great care in making the adjustments, to attain a sensibility of 90 divisions per volt. The readings in general are accurate to 0·02 of a volt, and they are pretty reliable to 0·01 volt.

§ 10. The experiments were continued with this improved apparatus, using plates of aluminium and platinum as the dissimilar metals. The P.D. between these metals measured as quickly as possible after cleaning the surface of the aluminium with fine emery-paper was

1·45 volts.

This value slowly fell as time went on*; thus after about $1\frac{1}{2}$ hours, it was

1·20 volts;

and it finally assumed, very slowly, a steady value of about

1·02 volts.

After this steady value had been arrived at, the experiment was proceeded with much as described in § 8. The tube was exhausted to about $\frac{1}{200}$ millim. pressure, and then heat was applied from two bunsen flames. The variations of pressure that followed were similar to those observed in the old apparatus (§ 8). Even after heating in this way for five hours the pressure was about the same as at the beginning of the operation (it varied from $\frac{1}{170}$ millim. to $\frac{1}{230}$ millim.), showing that after prolonged heating condensed air was still given off from the inside surfaces of the apparatus. This did not, of course, necessarily imply that there was still a large quantity of air left sticking to the metal plates, for as the heat slowly travelled up the tube by conduction air would be gradually driven off its upper surfaces, and this would continue until the whole of the apparatus (and even the pump) became strongly heated. The source of heat was very gradually removed, the pump being vigorously worked the whole time, until when the tube was quite cold the pressure was $\frac{1}{2500}$ millim. The P.D. between the plates was then

0·28 volt.

(I could never get a satisfactory reading until the tube was quite cold, for on insulating the platinum plate and its connected quadrants there was always a considerable leakage of electricity into the plate, possibly by convection from the surrounding gaseous molecules.)

After leaving the apparatus for 15 hours the pressure had risen to $\frac{1}{80}$ millim., and then the P.D. was

0·31 volt.

On exhausting to $\frac{1}{8000}$ millim. (without further heating) the P.D. was still

0·31 volt.

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* Erskine-Murray on "Contact Electricity of Metals," Proc. Roy. Soc. vol. lxiii. p. 124.

Air was then admitted into the tube. The reading remained unaltered even after several hours, but after leaving the tube open to the atmosphere for three days, the P.D. had fallen to

0·02 volt.

The aluminium plate was then taken out and very gently rubbed once or twice with fine emery-paper. The P.D. rose to

0·56 volt.

It was again rubbed with emery, after which the P.D. was

0·72 volt.

It is thus clear that at least the greater part of the above diminution of the contact effect was due to some change of surface of the aluminium plate, most probably oxidation, since it was a permanent effect and only removed by cleaning the plate, and also because almost the same phenomenon took place when the tube was heated under exactly the same conditions but in this case full of air, for on doing so the P.D. fell to

0·30 volt

when cold, and rose again to

1·10 volts

on thoroughly cleaning the aluminium.

§ 11. The experiments described in § 10 satisfied me that it was useless to attempt to drive off the last remnants of air from the metal plates by merely heating them in a vacuum, so I decided first to thoroughly wash out the apparatus three or four times with fairly pure dry hydrogen, and then strongly heat it in a high vacuum of that gas. I expected that such a molecularly active gas as hydrogen would displace even the last traces of air from the pores of the metal plates.

The hydrogen was prepared from fairly pure zinc (such as is used in Marsh's test for arsenic) and pure hydrochloric acid. It was washed by passing through distilled water and carefully dried by means of tubes of pumice and strong sulphuric acid and of phosphorus pentoxide. Such hydrogen should contain but the barest traces of foreign gases, and I considered it sufficiently pure for my purpose. (I had tried other methods of preparing the hydrogen, but found the above the most satisfactory on the whole. The chief thing was to avoid having such impurities in the gas as oxygen, ozone, water-vapour, or other oxygen-containing electrolytes.) There was probably a far greater quantity of strange gases in the vacuum-tube even after exhaustion than was in the hydrogen.

The hydrogen generating apparatus and drying-tubes were joined directly to the apparatus through a mercury-sealed tap. The generating apparatus, when not producing gas, was always kept full of hydrogen at a pressure greater than that of the atmosphere, so that if any leakage took place through the various joints it would be hydrogen leaking out into the atmosphere and not air leaking in.

§ 12. At the beginning of this new experiment the P.D. between the plates was

0·98 volt.

I exhausted to a vacuum of $\frac{1}{3000}$ mm., and let in hydrogen until the pressure was 1 atmosphere. The P.D. fell to

0·91 volt.

I then again exhausted to a pressure of $\frac{1}{200}$ mm., when the P.D. was

0·95 volt,

and again let in an atmosphere of hydrogen. The same operation was repeated a third time, and finally the apparatus was left to itself full of hydrogen for two days, so as to give the gas a good chance of soaking into the metals and displacing from them the original surface-layers of air. The voltage was then

0·87 volt,

and remained constant at that value. (This diminution is in accordance with Lord Kelvin's observation that soaking a platinum plate in hydrogen makes it temporarily about 0·1 volt positive to another platinum plate that has not been so treated.*)

I then again exhausted to $\frac{1}{5000}$ mm. and heated the tube with a couple of bunsen-burners just as on former occasions.

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* 'Nature,' April 4, 1881.

When cold the P.D. was

0·83 volt,

at a pressure of $\frac{1}{10,000}$ mm.

From the practical constancy of this value, it seemed to me that I had now really removed the last traces of air, and that there was not sufficient oxygen present to oxidize the aluminium plate as had happened before in an ordinary vacuum, and that there was a true contact P.D. between aluminium and platinum of about 0·8 of a volt. To subject it to the severest possible test, I next heated the apparatus to a far higher temperature with a blowpipe-flame. The outer copper protecting sheath was kept red hot for about half an hour, the pump working throughout the time. I then allowed the tube to slowly cool. When it was quite cold and the pressure was $\frac{1}{10,000}$ mm., the P.D. between the plates was

0·09 volt.

I let in a little hydrogen; it had no immediate effect on the P.D. I then let in dried air; the reading very slowly fell to zero, and the next morning it was

−0·15 volt

(*i. e.* aluminium negative to platinum), at which value it remained permanently. In appearance the aluminium was unaltered, except for a very slight purple coloration just at the bottom of the surface facing the platinum. Cleaning it well with emery-paper sent back the value to

1·20 volts.

Thus we have arrived at the exceedingly interesting fact that even in a *high vacuum of pure dry hydrogen at the minute pressure of* $\frac{1}{10,000}$ *mm. of mercury, and after four washings in that gas, there is still sufficient oxygen present to completely oxidize the surface of an aluminium plate,* if it only be brought to a sufficiently high temperature (about a dull red heat); and if there is sufficient oxygen present to oxidize it there is surely sufficient present to charge it as required by the electrolytic theory of the Volta effect.

In face of this striking experimental result, it is utterly futile to draw any positive conclusions whatsoever concerning the seat of the E.M.F. in Volta's phenomenon based on experiments made in what usually passes for a vacuum, whether it be a vacuum of air or one of any other gas; because, to repeat what I have already stated, unless far more drastic measures are taken—and no mere mechanical pumping will suffice—it is a matter of practical impossibility to remove the insoaked condensed air-films from the surfaces of such highly oxidizable metals as zinc and aluminium. And yet the most illustrious upholder of the contact theory asks concerning Dr. Bottomley's high-vacuum experiments (referred to above, § 1), made in a vacuum of $\frac{1}{523}$ mm. and without any application of heat, what would be the efficacy of the supposed oxygen bath in such a case! *

§ 13. In face of these results, a perfectly decisive experiment seemed almost hopeless to expect. However, I finally decided upon a method of removing the whole of the oxygen which really did offer some hopes of success, and that was to *chemically burn* away the oxygen. Such a process naturally could not be carried out with aluminium as the positive metal, simply because aluminium has a greater affinity for oxygen than has hydrogen, and it is impossible under any known circumstances to reduce aluminium oxide by means of hydrogen. Iron, however, was a metal that answered all the necessary requirements. The P.D. between it and platinum was sufficiently high (it varies from about 0·3 to 0·5 of a volt, according to surface conditions) for the purpose; the metal could be very strongly heated without fear of fusion or volatilization, and any oxide of iron present or formed in the process of heating could be easily reduced by hydrogen at a not unduly high temperature. There is another property possessed by iron which is of peculiar interest in connexion with these experiments, namely, its transparency to hydrogen at a red heat †. Owing to this remarkable and interesting property (which is likewise shared by platinum), it seemed probable in the highest degree that after the continued heating of such a platinum-iron couple in an atmosphere of hydrogen, the gas would freely permeate both metals and eventually combine with every trace of oxygen present,

* Phil. Mag. vol. xlvi. p. 82 (1898).

† Discovered by Graham: see his 'Collected Papers,' p. 279.

either directly or by reducing any iron oxide that has been formed, and the product of the combustion (water) would be driven off by the heat and absorbed in drying-tubes of phosphorus pentoxide. Of course I did not expect that all the oxygen would be removed in one operation; but that if the metals were brought to a red heat and then allowed to cool (both iron and platinum absorb hydrogen on cooling) and the operation repeated say half-a-dozen times, that little by little the whole or at least the greater part of the oxygen films condensed on the surface-layers of the metals would be driven off and replaced by hydrogen. Thus it would be possible to measure the contact P.D. between iron and platinum in an atmosphere of hydrogen and of *hydrogen only*. As has already been pointed out, it is useless to displace the outer atmosphere of hydrogen and to leave the inner layers of gas whose particles are within the range of molecular action of the metals unchanged (see § 1). From what follows (§ 14), I venture to think that as far as my experiments go they seem to confirm on the whole and within certain limits the series of phenomena that were suggested above as being likely to take place.

§ 14. The iron used was a piece of commercial sheet-iron. I should have preferred to use pure iron, but it would have had to be specially rolled, and as I was greatly pressed for time that operation would have taken longer than I could afford to wait.

In order to work with as large a P.D. as I could possibly get, I thoroughly cleaned and burnished the surface of the iron *; the P.D. between the burnished iron and platinum was

0·50 volt.

The next day it had fallen to

0·37 volt

(Dr. Erskine-Murray does not mention that the high potential produced by burnishing is merely a temporary effect), and remained practically constant at that value. I then exhausted and washed out the apparatus with hydrogen and repeated the process three times just as described in § 12. The tube was then heated with a blowpipe-flame and kept at a bright red heat for about 20 minutes. It was then, of course, full of hydrogen, at about an atmosphere pressure (when hot). Knowing the pressure of the gas in the tube both when it was hot and cold I was able, by making certain assumptions as to the distribution of heat, to roughly estimate the maximum temperature of the gas in the tube. After keeping the outside copper tube at a bright red heat for about 40 minutes the maximum inside temperature was not less than 800° C.

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* See Dr. J. Erskine-Murray, "On Contact Electricity of Metals," Proc. Roy. Soc. vol. lxiii. pp. 117–122.

The next morning the P.D. was

−0·40 volt (platinum positive to iron).

I then heated again, as before, for 33 minutes; when cold, after about three hours, the P.D. was

−0·06 volt.

I again heated for half an hour. The next morning the reading was

−0·28 volt.

I heated again for half an hour. After three hours the P.D. was

−0·05 volt.

I repeated the operation. The next day the P.D. was

−0·13 volt.

On again heating for half an hour the P.D., as measured after two hours' cooling, was

+0·05 volt.

I further heated for 35 minutes. In two hours and a half the P.D. was

−0·02 volt.

I heated again for half an hour. The next morning the voltage stood at

−0·16 volt.

I had hoped that after so many successive heatings and coolings the P.D. would have settled down to a steady value after all the oxygen had been got rid of, and that this value would be the true contact P.D. in an atmosphere of hydrogen. But, as is evident from the above readings, such was not the case; there seemed to be no tendency for the voltage to settle down to a final steady value. However, a careful examination of the above results and of others not given here, convinced me that there is a law underlying these results in spite of their apparently contradictory nature. It seems that, on the whole, readings that were taken as soon as possible after the heating (the tube, however, being cold or almost cold) were more positive (or less negative) than those taken some hours or on the next day after the heating. In order to test this supposition, when I next repeated the operation of heating, I took time-readings of the voltage, starting as soon as possible after the heating. There is really a double time effect taking place, the one superimposed upon the other: firstly, an ordinary temperature effect; this ceases when the tube is quite cold or soon after; secondly, the time effect particularly referred to here, which goes on, as will be seen, for several days, long after direct temperature effects have disappeared. In consequence of this the time-readings taken, say within the first two or three hours after heating, teach us nothing definite.

The tube was kept red hot for half an hour from 2.20 to 2.50 P.M., and then the asbestos-lined copper shield was immediately removed so as to allow it to cool as quickly as possible. At 3.30, when the apparatus felt almost cold, the P.D. was

0·18 volt.

At 3.50 it was	0·04 volt.
At 4.25 it was	−0·12 volt.
At 5	−0·15 volt.
At 8	−0·20 volt.

The next day at 10.30 A.M., −0·29 volt.

After two more days, at 10.30, −0·60 volt.

The temperature–E.M.F. curve becomes asymptotic at about −0·60 volt.

On repeating the operation by again heating and taking time-readings, I obtained very similar results. In this case the P.D. after twenty-three hours was

−0·28 volt,

and I then started exhausting the apparatus of hydrogen (although the equilibrium value, −0·60 volt, was not yet arrived at) with the intention of again letting air into the tube. When the pressure was $\frac{1}{330}$ mm. the P.D. was

−0·33 volt.

I then again let in a little hydrogen, 1 mm. merely; the P.D. immediately became relatively more positive, it being

−0·54 volt. (*Cp.* § 12 above.)

On again exhausting, the P.D. fell; when the pressure was $\frac{1}{100}$ mm. the reading was

−0·42 volt,

and at $\frac{1}{300}$ mm.

−0·35 volt,

just as before, at about the same pressure. I again let in a little hydrogen, this time 3 mm.; the P.D. became

−0·48 volt.

I then let in dry air, until the pressure was 1 atmosphere. The P.D. then moved slowly in the positive direction. The air was admitted at 6.35 P.M.

At 6.47 the P.D. was	−0·43 volt.
At 7.0 it was	−0·40 volt.
At 7.20	−0·37 volt.

The next morning at 10.30 it was

−0·17 volt.

This very slow return to the positive value, or, rather, in the positive direction, is just what one would have expected on the assumption that the Volta effect is a function of the medium surrounding the gases. Consider for a moment the state of the surfaces of the metals just at this juncture. The whole object of the experiment was to remove, to the utmost extent possible, the original condensed surface-layers of air from the plates, and to replace them by layers of hydrogen. From the method that was adopted, and from the results that followed, it is almost certain that this state was actually arrived at. Then the true contact P.D. between iron and platinum in an atmosphere of hydrogen *and hydrogen only* (neglecting for the moment the probably inactive nitrogen) is about −0·60 volt (platinum being positive to iron). The fact that this value was only reached long after the metals had cooled from a red heat in an atmosphere of hydrogen is easily explicable. The whole or greater part of the Volta effect is due to the layers of gas in immediate and close contact with the metal surfaces. Naturally, when the metals were hot, the amount of gas (in this case hydrogen) in such close contact was extremely small. As the metals cooled—and, indeed, long after they were cold—they were gradually soaking in and absorbing hydrogen; and all the time this was going on the P.D. was gradually becoming more and more negative (see p. 57), until at last the final value, about −0·60 volt, was reached, and this represents *the true value of the Volta effect between iron and platinum in an atmosphere of hydrogen.* When, then, I pumped out the hydrogen and let in air, the P.D. did not immediately return to its original positive value, although it slowly went back in the positive direction (no more than measuring the contact P.D. of air-covered plates of iron and platinum in hydrogen gives a P.D. of −0·60 volt) simply because the greater part of the gas in the closest contact with the metals was still hydrogen and not air. The metals would probably have to be left for months, and perhaps years, before the air would entirely replace the surface-layers of hydrogen. In fact, it would possibly be as difficult to replace the hydrogen-film by an air film as it was to displace the original air-film and replace it by hydrogen. Nevertheless, the all-important fact remains that a complete change of atmosphere, unaccompanied, as far as the chemical conditions enable us to judge, by any corrosion or oxidation of the metallic surfaces, induces a complete and fundamental change in the value of the Volta effect, differing not only in magnitude but also in sign from the first value. It would be well, if this experiment be repeated, to actually leave the metallic couple untouched for some considerable time (some weeks or even months if necessary) to see whether the maximum positive value of the P.D. would return of its own accord without external aid. In this case I thought I might hasten somewhat the process of replacing the new hydrogen-film again by an air-film by heating the tube. I kept the outside copper sheath red hot for about 15 minutes. When the tube was perfectly cold the P.D. was

$$+0{\cdot}22 \text{ volt.}$$

After two hours it remained entirely unaltered at 0·22 volt. It might be objected that heating in this way oxidized the iron; but it must be remembered that the plates were still partially surrounded with hydrogen, and before oxidation could take place the hydrogen would have to be driven off. (In any case, at a red heat any oxygen present would unite with the hydrogen rather than with the iron.) This view is supported by the result of a second heating, in this case extending over 20 minutes. Then, after the tube was cold, the P.D. was exactly zero, and on taking out the iron plate and examining it I found it completely covered with a thin black scale of iron oxide. There is no doubt, then, as to the effect of surface oxidation; and it is in agreement with other experimenters, who find that oxidation always causes the contact activity of metals to disappear.

§ 15. The net result of the experiments described above in § 14 is strongly in favour of that theory of the Volta effect which supposes it to be due to some electrolytic action of the medium or media surrounding the dissimilar metals *. We have seen how, by as far as possible removing the oxygen from the surfaces of an iron-platinum couple and replacing it by hydrogen, there resulted an enormous total change in the contact E.M.F., namely from +0·37 volt to −0·60 volt; how on again admitting air, so that a mixture of air and hydrogen surrounded the plates, the P.D. slowly moved in the positive direction, reaching after 16 hours a value of −0·17 volt; and how, after heating the plates so as to artificially hasten the removal of hydrogen from the surfaces

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* The supposed mechanism of this action I need not discuss here. Valuable and ingenious suggestions on this head have been made by Prof. Oliver Lodge in his Report to the British Association in 1884, quoted above, and they have been further elaborated in an interesting series of letters that passed between Prof. Lodge and Prof. Burnside in the columns of 'Nature,' vol. xliii.

of the metals and its replacement by air, the value of the P.D. became still more positive, namely +0·22 volt. There is a strong presumption of truth in the assertion that these curious variations in the contact force under varying conditions of atmosphere, which become so intelligible when looked at in the light of the electrolytic theory, appear impossible and incomprehensible when considered from a standpoint like that taken up by the pure contact theorists.

§ 16. This investigation does not in any way pretend to be final: it is hardly more than preliminary; but I venture to think that I have accomplished, or at least got near accomplishing, what has never before been attained in the history of contact electricity; namely, the entire removal (by chemical means) of the "ancient air-sheets" from the surfaces of the metals and making measurements in an entirely different medium, without at the same time permanently altering the surfaces of the metals by causing them to form salts (as happened, for instance, in the valuable experiments of Mr. J. Brown *). Unfortunately, circumstances compelled me to abandon this work for the time being, and thus prevented me from continuing experimental investigations in the same direction. But there are one or two experiments that might be suggested that could be very easily performed without any special expensive or complicated apparatus. Thus it would be very interesting to keep an iron plate red hot in a stream of pure dry hydrogen for several hours, allow it to cool in that gas, leaving it say for a few days, and then measure the contact P.D. between it and another iron plate that had not been so treated. This might be repeated with a platinum plate, and the two experiments together would then be somewhat equivalent to those described on pp. 56–58, and very much simpler to perform.

§ 17. It is with the hope that somebody will find it worth while to continue investigations along these lines, that I venture to publish these preliminary results †.

* Phil. Mag. Aug. 1878, and Feb. 1879.

† Since the above was written I am very pleased to be able to add that Mr. H. Tomlinson has now taken up the thread of this research, working for the present, with my old apparatus, and starting from the point at which I left off.

Throughout the whole of this work I have been fortunate enough to receive the valued assistance and advice of Prof. W. E. Ayrton, F.R.S., in whose laboratories at the Central Technical College the work was done, and of Mr. T. Mather, his Senior Demonstrator in the Physical Department. I must also thank my friend Mr. W. Duddell and Mr. W. T. Evans, who have so often kindly helped me, when necessary, in the experimental part of the work.

DISCUSSION.

Prof. LODGE said he had given the subject of contact electricity some attention fifteen years ago, and that the author had performed a valuable series of experiments, which are on the lines he should have liked to have tried himself at that time. He had always felt that a mere vacuum would never get rid of the condensed air-films. The burning-out process used had provided the most reliable results yet obtained in the subject.

Dr. LEHFELDT pointed out that the action of hydrogen upon ferric oxide was a limited one, and that it was impossible to bring about complete deoxidization in that manner, unless the hydrogen employed was completely freed from water-vapour.

Prof. PERRY said he had not been able to find time to study the paper, but expressed his interest in the experiments, and said they had not affected his opinion upon the nature of the Volta effect.

Prof. ARMSTRONG said he was not wholly satisfied with the results, although a substantial approach to a solution had been made. Although the author had fully realized how difficult such experiments were, he had treated the matter as a surface gas effect, and had not guarded against moisture. Gases must be both "dirty" and moist before chemical action can take place, and we cannot expect to arrive at a solution of the problem until we have removed not only oxygen, but "dirt" and moisture. It is impossible to completely exhaust an apparatus, and a number of molecules must always be left, more than necessary to produce the Volta effect; moisture can never be got rid of by exhaustion.

The method of Dewar, of using liquid oxygen or liquid hydrogen, would get rid of both gases and water-vapour, and in this manner it would be possible to perform experiments which could be regarded as final, although if the effect disappeared at low temperatures, it might perhaps be urged that the temperature was too low for it to be produced. In any case, the author must have been dealing with combination effects, for it had been proved that hydrogen alloyed both with platinum and iron at a dull red heat.

Mr. COOPER said he would like to see the experiments repeated in an atmosphere of nitrogen.

Prof. S. P. THOMPSON said he had recently taken part in a discussion upon the subject with some earnest followers of the old contact theory. They uphold that the property of metals which determines the potential difference when two are put in contact, is as fixed and definite as other physical properties, such as density ; and that the potential difference observed in air is approximately the same as the true potential difference. It has been agreed to call the former the apparent potential difference. Prof. Thompson said that, according to Pellat, the real Volta effect was near to the effect observed in air. In circuits formed of metals there are other electromotive forces of the order of a millionth of a volt. The chemical electromotive forces in a circuit are of the order of a volt, The value of the Volta effect, derived from thermodynamical considerations concerning the Peltier effect, is much smaller than observed chemical potential differences. If, however, we take into account, not only the Peltier effect, but also the Thomson effect, we shall have other terms entering into the equations, which may tend to give a value more nearly equal to a volt. Prof. Thompson said that, in observing chemical E.M.F.'s, the Peltier effects did not come into the question, because of their smallness compared with the value of the chemical effect.

Prof. PERRY pointed out that the Peltier effect was not distinct from the Volta effect, but was simply the differential coefficient of it.

Prof. LODGE said that if a circuit containing Peltier effects were treated thermodynamically, as if it were a reversible heat-engine, it was well known that there resulted an equation connecting the value of the Peltier effects with the rate of change of the whole electromotive force in the circuit with temperature. This electromotive force which changed was, however, not necessarily the Volta contact force.

Prof. PERRY said there was no need to imagine a new kind of contact effect.

Prof. AYRTON suggested that an advance might be made in the theoretical side of the question if the Chairman were to put in writing his objections to the statement that the E.M.F. concerned was the true Volta effect. The extent of the Peltier effect proves the variation of the Volta effect with temperature; but because it is small it does not necessarily follow that the Volta effect is small. Where the Volta effect is a maximum or a minimum, the Peltier effect vanishes. The experimental work of the paper did not go far enough to convince him of the nature of contact electricity. Before we can hope to prove anything with respect to the two theories, we must be able to get a cyclic change of events; that is to say, we must be able to change our surfaces and media in a perfectly definite manner, so as to be able at any time to return to the particular state from which we started.

Prof. EVERETT said that as the variation in the potential difference between two metals in a medium was probably due to slow chemical action, which caused the metals to become less and less susceptible, he should expect that changing backwards and forwards from one medium to another would give to the potential difference an oscillatory variation, gradually becoming smaller and smaller.

Prof. LODGE said that everyone would like to see experiments showing a cyclic effect as required by Prof. Ayrton, and that Mr. Spiers had made a step in that direction. The difficulty in these experiments is to avoid chemical action. Chemical action is not necessary to get the Volta effect. The effect would be greatest in dry gas; moisture tends to reduce or to abolish the effect.

Prof. CALLENDAR regarded the fact that the effect was profoundly modified by the condition of the exposed surfaces, but was quite independent of the actual surface of contact between the metals, as extremely interesting and significant.

Dr. Stansfield suggested gold as a suitable metal to be experimented on, because of its non-oxidizability.

Mr. J. Brown (communicated).—I agree, of course, with Mr. Spiers in considering that the Volta effect is due to chemically active films condensed on the metallic surfaces, but not that oxygen, correctly speaking, is the sufficient agent, since, as I have already pointed out*, there is reason to believe that these films must be of an electrolytic nature; therefore oxygen (uncombined) is insufficient.

If this be correct, the question arises whether Mr. Spiers' attempt to get rid of the oxygen by combining it with hydrogen would not result in the formation of a product eminently suited to assist in the formation of an electrolytic film, viz. water, thus tending to defeat the object in view.

In an admirably ingenious, novel and consistent set of experiments, C. Christiansen has recently shown † that the usual so-called "contact effect" is due to moisture in the atmosphere; it corresponds to the amount of moisture present and in oxygen which has been passed over phosphorous pentoxide and sulphuric acid; it is apparently reversed; the reversal being attributable to the formation of oxide films.

But even if we disregard the electrolytic view and consider the oxygen alone as active, and rely on heating and exhaustion for its removal, it would be more easily removed in the free state than as water, since oxygen is more volatile than water. If chemical absorption be relied on to get rid of active matters, I suggest that the resulting compound should be either a solid, as, for example, potassium hydrate, as in my last published experiments ‡, or, where exhaustion is used as an adjunct, something more volatile than the matter to be got rid of.

The application of heat to drive off active gases may be helpful in some respects. Hittorf § has, however, found that metals, even after having been kept at a red heat *in vacuo* for a long time, still retained occluded gas. A too high temperature involves the risk of the formation of protecting oxide or other compound layers on the surfaces of the metals. Indeed it would seem not unlikely that the very high difference of 0·6 volt described by Mr. Spiers in § 14 might be due to some such surface-layer on the iron in conjunction with the hydrogen-saturated platinum plate. (Iron, as I have before pointed out*, is peculiarly liable to the formation of such protecting films.) Such a supposition would agree with the fact observed in § 14 that a fall of potential in the platinum side of the couple always followed evaporation of the hydrogen from the platinum either by heating or exhaustion or in its slow removal by dried air.

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* Proc. Roy. Soc. vol. xli. (1886) p. 294.

† Wied. *Ann.* vol. lxix. (1899) p. 662.

‡ Proc. Roy. Soc. vol. lxiv. (1899) p. 370.

§ Wied. *Ann.* vol. vii. (1879) p. 574.

It will be observed that while Mr. Spiers assumes the 0·6 volt arises from simply an iron-platinum couple in pure hydrogen, I take it that we have on one side a platinum-hydrogen alloy coated with an electrolytically active film, and on the other an iron surface protected from its film by slight tarnish due to heating before it was quite free from oxidizing matters. In conjunction with this it is to be noted that as Mr. Spiers heated only the lower part of his tube, it may be supposed that there remained, condensed on the cooler surfaces, moisture films which on the cooling of the metals diffused towards them and condensed on them.

In such experiments the employment of a gas so chemically active as hydrogen seems undesirable, and I have long since concluded that if one seeks a zero result the atmosphere employed should have zero activities; the nearest approach to this characteristic being found in nitrogen.

Although my estimate of the conclusions to be drawn from these experiments may differ from that of their author, I think his painstaking work is to be welcomed as clearing the ground and as evidence of the extreme difficulty of getting rid of active gas. In the last respect it is consoling to others who have tried other means only to find the same difficulty. In this connexion I have sometimes doubted if glass is quite impervious to gases.

Mr. Spiers refers (§ 16) to an objection to my former experiments on account of complications introduced by alteration of the metallic surfaces. The same objection has been raised by others, including Professors Ayrton and Perry in 1881; and in reply I pointed out * "that in the copper-iron ring experiments though, after admission of the hydrogen sulphide gas, the copper side becomes strongly positive to the iron, very soon this difference of potential *diminishes and finally disappears* if the experiment be continued sufficiently long. . . . . . . If the potential difference is due to 'contact action' between the metals, their sulphides and the surrounding gas, why does it disappear while all these conditions are still present?"

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* Proc. Roy. Soc. vol. xli. (1886) p. 298.

Mr. Spiers, in replying, referred to Dr. Lehfeldt's assertion that the whole of the oxygen cannot be removed by hydrogen. In his experiments, however, there was very little ferric oxide and a large quantity of hydrogen, and although it was possible that all the oxide was not reduced, still a large portion of it was. The point to be particularly noticed was the fact that both the iron and the platinum being transparent to hydrogen at a red heat, they became thoroughly permeated with that gas, so that the gaseous film that was finally in closest contact with the plates was hydrogen, and not, to any great extent, air. The experiments were to be carried on, and attempts would be made to get a cyclic effect.

(*Added March 26th*, 1900.)—Mr. Brown's remark (p. 65) that oxygen would be more easily removed from the metal surfaces than water is hardly true, under the conditions obtaining in my experiments. In fact, the whole point of the investigation is that only the presence of a highly oxidizable gas such as hydrogen prevents the oxygen in the surface-layer from combining with the metals when they are strongly heated. Experiments in a perfectly inert gas, such as nitrogen, would probably turn out to be useless, for it could not burn away the original oxygen from the metal surfaces. Mr. Brown's interpretation of my results does not upset my main contention, that changing the atmosphere in closest contact with the metals effects a radical and fundamental change in the contact P.D. between them.

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* Phil. Mag. vol. xi. (1881) p. 212.

III. *On the Conductivities of certain Heterogeneous Media for a Steady Flux having a Potential.* *By* CHARLES H. LEES, *D.Sc.**

IN the chapter on "Conduction through heterogeneous media," in his 'Electricity and Magnetism,' Maxwell works out the conductivity of a compound medium formed by embedding in a medium of conductivity k_2 a number of small spheres of a medium of conductivity k_1, for the case in which the total volume of the spheres bears only a small proportion to that of the medium k_2, and the distances of the spheres apart are so great that they have no mutual effect on one another. He also works out the conductivities for two other cases of compound media: in the first the two media are separated by planes either parallel or perpendicular to the plane equipotential surfaces in the media; in the second the parts of the two media consist of right prisms of rectangular cross-section, one dimension of the cross-section being infinitely great compared to the other, and the length of each prism being again infinitely great compared to this greatest cross-sectional dimension, placed with their edges either parallel or perpendicular to the equipotential surfaces. The difference of order of magnitude of the three dimensions of the elementary prisms of the two media in this last case is necessary in order that the disturbance of the flow near the edges of the prisms may be neglected in the calculation.

These three cases, although of considerable interest, have only a limited application on account of the restrictions introduced to enable the calculations to be carried out; and I propose here to consider the case of a medium formed of an equal number of infinitely long prisms of square cross-section, of two media having conductivities k_1 and k_2, arranged as shown in fig. 1, and bounded by two parallel equipotential planes, AB, CD, drawn through the diagonals of the cross-sections of the prisms.

I assume that the flux and potential are continuous at the surfaces of separation of the two media. If, as in the case of the electrical potentials of copper and zinc, a difference of potential may exist between the media on the two sides of the surface of separation without a flux resulting, the potential which is continuous through the surface must be understood to be that to which the flux is due.

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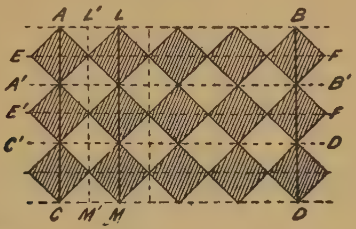
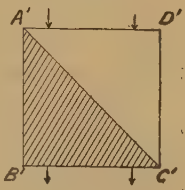
* Read November 24, 1899. (Communicated by Mr. Watson.)

Fig. 1.



From symmetry it is evident in the first place that A′B′, C′D′, and in the second place that EF, E′F′, &c., are equipotential planes. Also that AC, BD, LM, L′M′, &c., are lines of flow. Hence the problem is reduced to finding the conductivity of a prism of square cross-section A′B′C′D′ (fig. 2), of which A′D′ and B′C′ are equipotential surfaces, A′B′ and D′C′ lines of flow, and A′B′C′ consists of a medium of conductivity k_2, A′D′C′ of a medium of conductivity k_1.

Fig. 2.



If v_1 and v_2 are the potentials in the two media respectively, each satisfies the general condition

$$\frac{\partial^2 v}{\partial x^2}+\frac{\partial^2 v}{\partial y^2}=0\,;$$

v_1 becomes equal to a constant along A′D′, and has no flux across D′C′; v_2 becomes constant along B′C′, and has no flux across A′B′; v_1 and v_2 become identical along, and the fluxes due to them equal across, A′C′.

It might be possible to construct two functions which would satisfy these conditions by adding together particular solutions of the above equation of the form $v=e^{a(x\pm iy)}$, in the way done by Riemann*; but it is easy by a change of coordinates to make the problem depend on the following simple case, the solution of which is known.

Let AC (fig. 3) be the line of separation of two media of conductivities k_1 and k_2, and let AD be an equipotential and DC a stream-line in the k_1 medium. Let k_1/k_2 have such a value that AB, the stream-line in the second medium passing through A, makes the same angle with AC that AD does. If, then, CB is the equipotential line in the second medium passing through C, the triangle ABC is equal to the triangle ADC.

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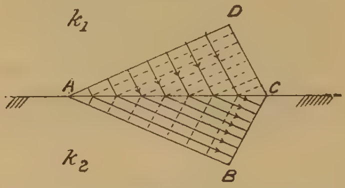
* *Partielle Differentialgleichungen*, Abschnitt iv., Bewegung der Wärme.

Fig. 3.



If z is the vector coordinate of a point in the plane of fig. 3, and z' the vector coordinate of a point in the plane of fig. 2, it is possible by a transformation $z'=f(z)$ to convert the right-angled triangle ADC in the z-plane into the isosceles right-angled triangle A′D′C′ in the z'-plane *. The same transformation † converts similarly the triangle ABC in the z-plane into the triangle A′B′C′ in the z'-plane; and contiguous points on opposite sides of AC in the z-plane become contiguous points on opposite sides of A′C′ in the z'-plane. Hence the quadrilateral ABCD converts into the quadrilateral A′B′C′D′, and the difference of potential and the amount of the flux between any two points of the area ABCD will be identical with the quantities for the corresponding points of the area A′B′C′D′.

If V is the difference of potential between the points A, C of fig. 3 and AC$=a$, the flux bounded by the stream-lines DC and AB

$$=k_1\frac{a\cos\theta\,\mathrm{V}}{a\sin\theta}=k_1\mathrm{V}\cot\theta,\text{ where }\theta=\angle\,\mathrm{DAC}.$$

Hence the flux bounded by the stream-lines D′C′ and A′B′ in fig. 2 under the potential-difference V is equal to $k_1\mathrm{V}\cot\theta$.

If k is the apparent conductivity of the square, the flux bounded by the stream-lines D′C′ and A′B′ is equal to $k\mathrm{V}$; hence

$$k_1\mathrm{V}\cot\theta=k\mathrm{V},\quad\text{or}\quad k=k_1\cot\theta.$$

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* Forsyth, 'Theory of Functions,' p. 543; Love, Amer. Journ. of Math. xi. pp. 164 & 168 (1889).

† If in $z=x+iy$, x is taken along, and y perpendicular, to AC.

Now in fig. 3, since the flux is continuous across AC, $k_1 \cot \mathrm{DAC} = k_2 \cot \mathrm{BCA}$. Also $\angle \mathrm{BAC} = \angle \mathrm{DAC}$.

$$\therefore\ k_1 \cot \theta = k_2 \tan \theta ;$$

$$i.e.\ \ \cot \theta = \sqrt{\frac{k_2}{k_1}}.$$

Therefore the apparent conductivity k of the square

$$= \sqrt{k_1 k_2}.$$

If now this medium, consisting half of material k_1, half of material k_2, be supposed homogeneous, and be combined, in the way indicated in fig. 1, with an equal volume of the k_1 medium, we have k' the conductivity of the new medium,

$$= k^{\frac{1}{2}} k_1^{\frac{1}{2}},$$

$$= k_1^{\frac{3}{4}} k_2^{\frac{1}{4}}.$$

Similarly, by making other combinations of the new media and the old, we deduce that if a volume p_1 of a medium of conductivity k_1 be combined in this manner with a volume $1-p_1$ of a second medium of conductivity k_2, the conductivity k of the combination will satisfy the equation

$$k = k_1^{p_1} k_2^{(1-p_1)} ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\log k = p_1 \log k_1 + (1-p_1) \log k_2,$$

$$= \log k_2 + p_1 \log \frac{k_1}{k_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

That is, for the mixture considered, the logarithms of the conductivities for fluxes parallel to the diagonals in fig. 1 follow the law of means.

Since $\log k = -\log \rho$, where ρ is the resistivity of a medium, we also have

$$\log \rho = p_1 \log \rho_1 + (1-p_1) \log \rho_2$$

$$= \log \rho_2 + p_1 \log \frac{\rho_1}{\rho_2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as the relation between the resistivity of the mixture and the resistivities and relative volumes of its constituents.

If more than two media are present in volumes p_1, p_2, p_3, &c. per c.c. of the mixture,

$$k = k_1^{p_1} \,.\, k_2^{p_2} \,.\, k_3^{p_3} \ldots\ldots \quad . \quad . \quad . \quad . \quad (4)$$

In order to show the principal features of the distribution of the flux and potential in a medium consisting of equal square prisms of two media arranged as indicated in fig. 1, the equipotential lines (or the stream-lines) for the single block considered above are shown in fig. 4, and for a strip of the medium in fig. 5. In each case one constituent conducts six times as well as the other. The curves have been drawn by an approximate method which depends on the fact that near each angular point A, C, the equation which tranforms the kite-shaped figure of fig. 3 into the square of fig. 2 takes the form $z'=Az^n$. The accuracy of the diagrams will therefore be least near the centre of each square ABCD, where the position of an equipotential line may be in error by 10 per cent. of its distance from the next one.

Fig. 4.

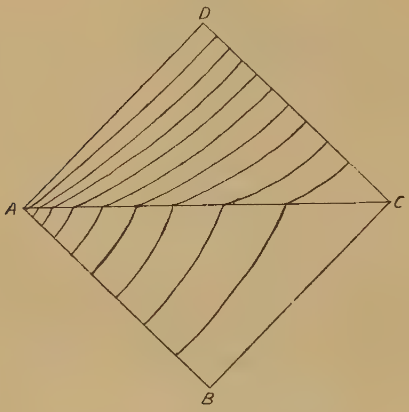
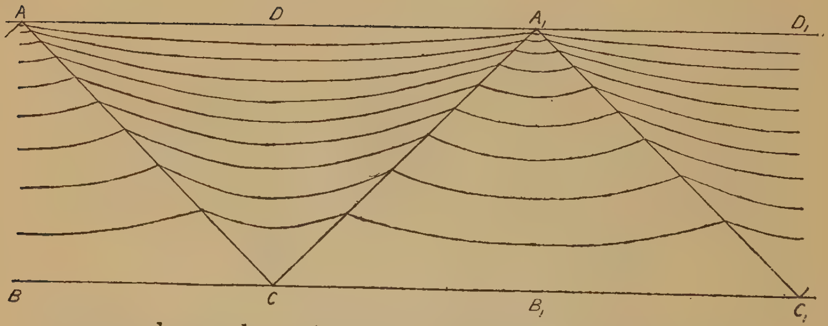


Fig. 5.

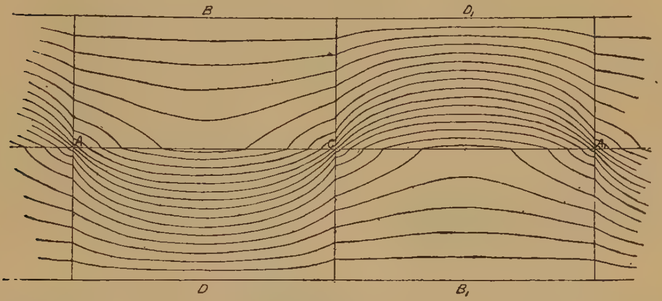


Professor Lamb has pointed out to me that by superposing a second flux, the direction of which is at right angles to the first, on the first, a flux with stream and equipotential lines through the centres of the squares parallel to their sides is obtained. The conductivity of the medium for this flux will be readily seen to be given again by the formula

$$k=\sqrt{k_1k_2}.$$

The equipotential lines (or the stream-lines) for a strip of the medium, when one constituent conducts six times as well as the other, are shown in fig. 6.

Fig. 6.



Since there are four directions of flow in the medium for which the conductivity has the above value, the conductivity of the medium when fine-grained will have the same value for a flux in any direction ; *i. e.* equation (4) gives the conductivity of a compound medium in the general case where the constituents are present in the form of long prisms with their axes perpendicular to the planes of flow.

IV. *On the Thermal Conductivities of Mixtures and of their Constituents.* By Charles H. Lees, *D.Sc.*[*]

Those physicists who have endeavoured to express the thermal conductivities of physical mixtures in terms of the conductivities of their constituents, and the amount of each present, have made use of the formulæ

$$k=\frac{p_1k_1+p_2k_2}{p_1+p_2}, \quad \ldots \ldots \quad (1)$$

$$\frac{1}{k}=\frac{p_1\frac{1}{k_1}+p_2\frac{1}{k_2}}{p_1+p_2}, \quad \ldots \ldots \quad (2)$$

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[*] Read November 24, 1899.

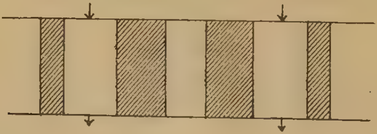
where k_1 and k_2 are the conductivities of the constituents, and p_1 and p_2 either the masses or the volumes of each present. Paalhorn, Winkelmann, and Schott, in their paper on the conductivities of glasses *, used the first form with the p's the masses of the constituents present; but Winkelmann has recently recalculated the results †, using the second form, with the p's the volumes of the constituents present, and found a better agreement than formerly.

Focke ‡ uses the first formula, with the p's the masses, to represent his own results on the conductivities of various kinds of glass. Both theory and experiment §, however, point to the conclusion that it is the proportion by volume which ought to be used in such calculations; and I shall confine myself in what follows to the consideration of the proportions by volume, calculated on the assumption that the mixture is simply a physical mixture, and is formed without contraction. Under these conditions the formula

$$k=\frac{p_1k_1+p_2k_2}{p_1+p_2}$$

corresponds to the constituents being distributed in the space between the two parallel isothermal surfaces through which the heat enters and leaves the medium, in the form of right prisms with their axes perpendicular to these surfaces, thus :–

Fig. 1.



and the formula

$$\frac{1}{k}=\frac{p_1\frac{1}{k_1}+p_2\frac{1}{k_2}}{p_1+p_2}$$

to their being distributed in layers parallel to the isothermal surfaces, thus :—

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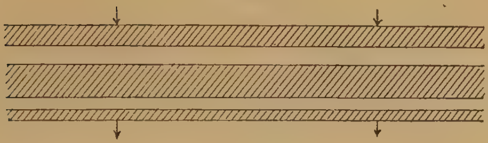
* Wied. *Ann.* li. p. 738 (1894).

† *Ibid.* lxvii. p. 160 (1899).

‡ *Ibid.* lxvii. p. 155 (1899).

§ Lees, Phil. Trans. Royal Society, cxci. p. 433 (1898); *ante*, p. 70.

Fig. 2.

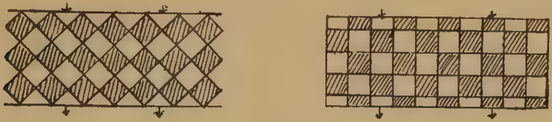


It has been recently shown * that the formula

$$\log k = \frac{p_1 \log k_1 + p_2 \log k_2}{p_1 + p_2} \quad . \quad . \quad . \quad . \quad (3)$$

corresponds to a prismatic distribution which, in the case of equal volumes of the constituents being present, is represented in section thus:—

Fig. 3.



As one cannot assume that one of these three distributions is more likely than another to represent the actual facts, I propose to apply each of the three formulæ to the calculation of the conductivities of the mixtures of solids and liquids experimented on by G. Wiedemann †, Henneberg ‡, and myself §, and compare the results of the calculations with the values found experimentally.

It will be noticed that the conductivities determined for successive equal increments of one constituent, correspond for the first formula to the successive terms of an arithmetic, for the second to the terms of a harmonic, and for the third to those of a geometric series, the first and the last terms of the three series being the same. The third formula will therefore give a value for the conductivity of a given mixture between the values given by the first and second formulæ. In the tables which follow the values calculated by the three formulæ (1), (2), and (3) are referred to as "mean conductivity," "mean resistivity," and "mean logarithmic" respectively.

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* Lees, *ante*, pp. 72–73.

† G. Wiedemann, Pogg. *Ann.* cviii. p. 393 (1859).

‡ Henneberg, Wied. *Ann.* xxxvi. p. 146 (1889).

§ Lees, Phil. Trans. Royal Soc. cxci. p. 399 (1898).

Tin-Bismuth Alloy * (Wiedemann).

Composition by volume.	*k* observed, Ag=100.	*k* calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Sn	15·2						
„ 20 p. c. Bi	10·1	12·5	+ 24	6·1	−40	9·9	− 2
„ 42·7 p. c. Bi ...	5·6	9·5	+ 70	3·6	−36	6·1	+11
„ 69·1 p. c. Bi......	2·3	5·9	+156	2·5	+ 8·7	3·5	+52
Bi	1·8						

Dilute Ethyl Alcohol (Henneberg).

Composition by volume.	*k* obs.	*k* calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Water	100						
„ 12·4 p. c. Ethyl Alc....	91	91·3	+ 3	78·0	−14	86·1	− 5·4
„ 24·5 „ „ ...	81·4	82·9	+ 2	63·8	−22	74·5	− 8·5
„ 36·1 „ „ ...	73·1	74·8	+ 2	54·4	−26	64·9	−11
„ 47·3 „ „ ...	64·6	66·9	+ 4	47·7	−26	56·8	−12
„ 57·8 „ „ ...	54·6	59·6	+ 9	42·7	−22	50·0	− 8
„ 67·7 „ „ ...	47·6	52·7	+11	38·9	−18	44·4	− 7
„ 76·9 „ „ ...	41·7	46·3	+11	35·9	−14	39·7	− 5
„ 85·4 „ „ ...	37·5	40·3	+ 7	33·5	−11	35·9	− 4
„ 93·2 „ „ ...	32·1	34·9	+ 9	31·6	− 2	32·7	− 2
Ethyl Alcohol	30·1						

Water and Glycerine.

Water	·00140						
„ 20·8 p. c. Glycerine ...	119	125	+ 5	116	−3	121	+2
„ 44·2 „ „ ...	101	109	+ 8	97	−4	103	+2
„ 70·4 „ „ ...	81	91	+12	82	−1	86	+6
Glycerine	70						

Water and Ethyl Alcohol.

Water	·00149						
„ 30 p. c. Alcohol	104	118	+13	99	− 5	105	+1
„ 58 „ „	79	90	+14	66	−16	76·4	−3
„ 81 „ „	59	60	+12	54	− 8	58·5	−1
Ethyl Alcohol	47						

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* Wiedemann's copper-zinc results appear to exclude this alloy from the class of physical mixtures.

Water and Acetic Acid.

Composition by volume.	*k* obs.	*k* calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Water	·00149						
„ 24 p. c. Acetic Acid	118	124	+ 5	94	−20	110	−7
„ 48·7 „ „	88	97	+10	68	−23	82	−7
„ 74 „ „	64	71	+11	53	−17	59	−8
Acetic Acid	43						
Water and Methyl Alcohol.							
Water	·00148						
„ 28·8 p. c. Meth. Alc.	111	120	+ 8	97	−13	109	−2
„ 58·0 „ „	80	92	+15	71	−11	81	−1
„ 80·7 „ „	63	70	+11	59	− 6	64	−1
Methyl Alcohol	52						
Ethyl Alcohol and Glycerine.							
Ethyl Alcohol	·00044						
„ „ 17·4 p. c. Glyc.	43	49	+14	47	+9	48	+12
„ „ 38·7 „ „	50	54	+ 8	51	+2	53	+ 4
„ „ 65·3 „ „	56	61	+ 9	58	+4	60	+ 7
Glycerine	70						
Methyl Alcohol and Ethyl Alcohol.							
Methyl Alcohol	·00052						
„ „ 25 p.c. {Ethyl Alc.}	5	505	+1	505	+1	505	+1
„ „ 50 „ „	47	49	+4	49	+4	49	+4
„ „ 75 „ „	46	475	+3	47	+2	475	+3
Ethyl Alcohol	46						
Vaseline and Marble.							
Vaseline	·00044						
„ 25 p. c. Marble	63	210	+233	57	−10	88	+40
„ 43 „ „	108	330	+206	74	−31	145	+34
„ 60 „ „	179	444	+149	102	−43	234	+31
Marble	710						
Lard and Zinc Sulphate.							
Lard	·00047						
„ 23·8 p. c. $ZnSO_4$	59	60	+ 2	56	− 5	61	+3
„ 37·5 „ „	74	84	+14	63	−15	72	+3
„ 55·5 „ „	84	101	+20	75	−11	88	+5
Zinc Sulphate	145						

Without endeavouring to express the relative values of the three formulæ numerically, we may arrange the three in order of merit for each mixture as follows :—

	Order of merit of calculated Values.		
	Best.	Middle.	Worst.
Water and Ethyl Alcohol (Henneberg)	Conductivity. Logarithm.	....	Resistivity.
Water and Ethyl Alcohol (Lees)	Logarithm.	Resistivity.	Conductivity.
Water and Glycerine	Resistivity.	Logarithm.	Conductivity.
Water and Acetic Acid	Logarithm.	Conductivity.	Resistivity.
Water and Methyl Alcohol.	Logarithm.	Resistivity.	Conductivity.
Ethyl Alcohol and Glycerine	Resistivity.	Logarithm.	Conductivity.
Ethyl Alcohol and Methyl Alcohol	Resistivity.		Conductivity. Logarithm.
Tin and Bismuth (Wiedemann)	Logarithm.	Resistivity.	Conductivity.
Vaseline and Marble	Resistivity.	Logarithm.	Conductivity.
Lard and Zinc Sulphate	Logarithm.	Resistivity.	Conductivity.

From this it will be seen that the formula

$$k=\frac{p_1k_1+p_2k_2}{p_1+p_2}$$

represents the observed results worst, and that of the other two the formula

$$\log k=\frac{p_1\log k_1+p_2\log k_2}{p_1+p_2}$$

is somewhat better than

$$\frac{1}{k}=\frac{p_1\frac{1}{k}+p_2\frac{1}{k_2}}{p_1+p_2}.$$

The representation of the observed facts which even the best of the three gives is, however, only rough. As a rule the mean resistivity formula gives too low, and the mean logarithmic formula too high, values for the conductivity of each mixture. Now the conductivity of a compound built up of two materials, as in fig. 3, but with the same structure repeated in a plane perpendicular to that of the drawing, *i. e.* consisting of cubes of the two media, will be greater than that of the prisms of fig. 3, and will therefore deviate more from the value of the conductivity found experimentally than does that given by the logarithmic formula. Hence it seems unnecessary to attempt an accurate calculation of the conductivity of the mixture of cubes. Since the deviations from the calculated values found in the cases considered in the above tables also appear to differ in character from one mixture to another, it may be concluded that the thermal conductivity of a mixture is not completely determined by the conductivities of its constituents, and by the volume of each constituent present.

The attempts which have hitherto been made to represent the thermal conductivity of glass as a function of its composition and of the unknown conductivities of its constituents, must therefore be considered as not justified by our knowledge of the behaviour of mixtures of substances the conductivities of which are known.

The formula expressing the conductivity of a mixture in terms of its composition and the conductivities of its constituents, must then contain at least one quantity dependent on the characters of the two constituents, and three of the calculated values of the conductivity may be made to coincide with the observed values. There are many empirical formulæ which under these conditions give values that agree fairly well with the intermediate observations; and although I have found the formula

$$k^n = \frac{p_1 k_1^n + p_2 k_2^n}{p_1 + p_2}, \quad \ldots \ldots \ldots \quad (4)$$

where n is an arbitrary constant, on the whole satisfactory, the material at our disposal for testing the relative values of the various empirical formulæ which might be suggested, is not yet sufficient to warrant the selection of any one of them as the best representation of the thermal conductivity of a mixture.

The result of this examination may then be summed up as follows :—

Of the three values for the conductivity of a mixture calculated from the mean conductivity, mean resistivity, and mean logarithmic formulæ, that from the mean conductivity is most unsatisfactory, and that from the mean logarithmic formula least unsatisfactory. The logarithmic formula gives in general too high, and the resistivity formula too low a value for the conductivity.

The conductivity of a mixture appears not to be dependent solely on the volume and conductivity of each constituent present.

The empirical formula (4) gives a fair representation of the observations in the preceding tables.

DISCUSSION.

Mr. APPLEYARD pointed out that it was frequently of importance to be able to calculate the specific resistance of a mixture of dielectrics from the known specific resistances of the components. He had attempted to do this by means of the old formulæ, but with only approximate success; the one gave a result too low, and the other a result too high. He expected improved results by applying Dr. Lees' formula to such a case. Moveover, from the nature of the problem, Dr. Lees' formula should enable the specific capacity of a dielectric mixture to be calculated from the specific capacities of its components; this was of great practical importance in the manufacture of cable-core.

Mr. CAMPBELL said that the difference between the calculated and observed results might be due to the thermoelectric properties of the materials. Lord Rayleigh had observed that the high resistivity of alloys might be due to a back E.M.F. due to the Peltier effect at the junction of dissimilar metals. Mr. Campbell said that he had measured the resistances of ferro-nickel both with direct and alternative currents, and found them the same in the two cases, although iron and nickel are widely apart on the thermoelectric diagram.

V. *On Obliquely-crossed Cylindrical Lenses.*

By Silvanus P. Thompson, *D.Sc., F.R.S.*[*]

Cylindrical lenses have not claimed much attention from writers on geometrical optics. Certain of their properties, which make them invaluable to the ophthalmic surgeon for the correction of astigmatism, are, however, considered in all modern treatises on ophthalmics. Airy applied them for this purpose, but Donders first treated them systematically, in 1862, in his work *Astigmatismus und cylindrische Gläser*. Reusch in 1868 published his *Theorie der Cylinderlinsen*. Javal has written much on the subject from the ophthalmological point of view, as has Mr. S. M. Burnett. Mr. C. F. Prentice has also written of them in two works, a 'Treatise on Ophthalmic Lenses' and 'Dioptric Formulæ for combined Cylindrical Lenses.' Stokes[†] has proposed a cylindrical lens of variable power by combining at a variable angle two equal cylindrical lenses of opposite sign. The problem of the optical properties of crossed cylindrical lenses was touched upon by Reusch and by Donders. Krüss has written upon the aberration of "bicylindrical" lenses, meaning by that term such lenses as have both surfaces cylindrical and of equal curvature, but with their axes mutually at right-angles. Lastly, Prentice has given very elaborate rules for calculating the equivalent sphero-cylindrical lens for any combination of two lenses crossed at any angle. The importance of the solution of this problem arises from a point in modern ophthalmic practice:—In cases of ordinary astigmatism in which the refractive power of the eye is different in different meridians around the optic axis. One process of examination of this defect consists in ascertaining the position of the meridian of greatest refractive power, and in then measuring that power; and, this having been done, measuring the power in a meridian at right angles to the former, that is to say in the meridian of minimum refractive power. The difference between these two powers gives in reality the amount of cylindricity to be corrected. Or the excess of each over the normal spherical refractive power of the eye might be separately corrected by the choice of two appropriate cylindrical lenses which are then superposed at right angles. Sometimes, however, ophthalmic surgeons, whether through insufficient appreciation of the geometrical and optical principles involved, or through some incidental cause, prescribe a lens with two cylindrical curvatures on the respective faces of the lens, not crossed at right-angles but at some oblique angle. As such lenses are difficult of manufacture, and as their optical effect can be precisely reproduced by a suitably calculated and more readily ground sphero-cylindrical lens, the optician desires to have simple rules for calculating the equivalent sphero-cylinder. Hence the present attempt to arrive at easier rules for obliquely-crossed cylindrical lenses. To establish these rules it is possible to proceed by a simpler method than that of Reusch, whose investigation is exclusively based upon the properties of parabolic lenses.

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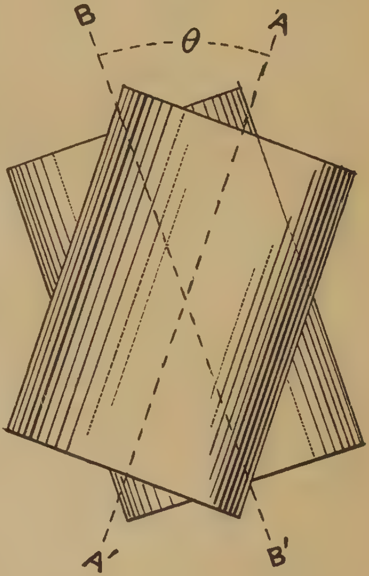
[*] Read December 8, 1899.

[†] Mathematical and Physical Papers, vol. ii. p. 172.

Fig. 1.



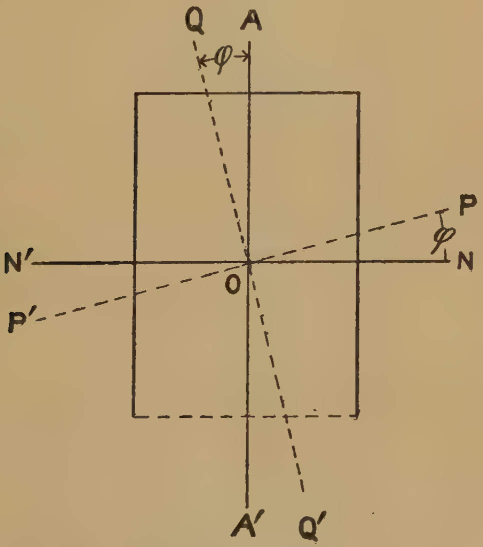
2. In the case of thin cylindrical lenses it is customary to call a line drawn through the lens, in a direction parallel to the axis of the generating cylinder of which its curved surface forms a part, "the axis" of that cylindrical lens. Let there be two thin cylindrical lenses placed in contact behind one another, so that their axes A A′, B B′ make an angle θ with one another. The optical axis of the system passes through their intersection and is normal to the plane containing them. It is required to find the combination consisting of one thin cylindrical lens and one spherical lens which will be the optical equivalent of the system; or, the sphero-cylindrical lens that

is also equivalent. The problem is completely solved when we shall have ascertained the two components, cylindrical and spherical, of the equivalent lens and the angular position of the cylindrical component.

In any lens having at one surface a radius of curvature r, the curvature which that surface will impress upon a plane wave is $(\mu-1)/r$; where μ is the refractive index of the material. If the lens is cylindrical, having a curvature in one meridian only, the impressed curvature will also be cylindrical; if it be spherical, the impressed curvature of the wave-front will be correspondingly spherical. First approximations only are here considered.

Let (fig. 2) A A′ be the axis of a cylindrical lens, and

Fig. 2.

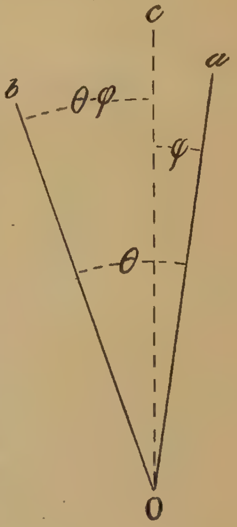


N N′ a line normal to that axis. A plane normal to the axis intersecting the lens in N N′ will have as its trace through the curved surface of the lens a line of the same curvature as the lens, viz. $\frac{1}{r}$. Let now an oblique intersecting plane be drawn through the optic axis of the system (*i. e*, the line through O normal to the plane of the diagram); its intersection P P′ making an angle N O P $\equiv \phi$ with the line N N′. The curvature at O of the trace of this plane, where it cuts the curved surface along P P′, will be $\frac{1}{r}\cos^2\phi$. This follows from the circumstance that P P′ is part of an ellipse whose major and minor axes are respectively $r/\cos\phi$ and r. We may further consider the intersection Q Q′ of another oblique plane at right-angles to P P′. The curvature at O along the line Q Q′ will be $\frac{1}{r}\sin^2\phi$. The sum of these two curvatures will obviously be equal to the original maximum curvature along N N′, since the minimum curvature along A A′ is zero. Hence we may regard the curvature along N N′ as contributing two components of cylindricity of the respective values named in the two directions P P′ and Q Q′. If light were admitted through narrow parallel slits set respectively along P P′ and Q Q′, the convergivity of the two beams respectively impressed by the lens would be $(\mu-1)\cos^2\phi/r$ and $(\mu-1)\sin^2\phi/r$. If r is expressed in metres, these two convergivities will be expressed in dioptries according to the practice now internationally adopted by ophthalmists.

It is obvious that the angle ϕ may be measured either between N N′ and P P′, or between A A′ and Q Q′.

3. Returning to the problem enunciated with reference to fig. 1, we may now find a solution by resolving each of the two cylindrical lenses into components and then recombining these components in the manner presently to be considered.

Fig. 3.



Let the line O a (fig. 3) represent the direction of the axis of one of the given cylindrical lenses, having a power of A dioptries, and the line O b the direction of the axis of the other given cylindrical lens of power B dioptries. The angle θ between O a and O b is also given. It is required to find the respective number of dioptries C and D of the cylindrical and spherical lenses which shall together constitute a combination whose optical effect is the equivalent of that of A and B. It is also required to find the angular position of the axis of the equivalent cylindrical lens.

It is clear that we might take any line O c through O making an angle ϕ with O a, and take the cylindrical components, along that direction, of the two given cylindrical lenses A and B. The sum of these components would be $A \cos^2 \phi + B \cos^2 (\theta - \phi)$. Similarly there might be taken, at right-angles to O c, the two other cylindrical components, whose sum would be $A \sin^2 \phi + B \sin^2 (\theta - \phi)$. Now there will be in every case one particular value of ϕ which will make the former sum a maximum and the latter a minimum. If we can find this value of ϕ, the problem is solved.

Differentiating with respect to ϕ the expression above obtained for the sum of the two components along O c, and equating to zero, we find that when this sum is a maximum the angle ϕ will be such as to give the relation

$$\frac{A}{B} = \frac{\sin 2(\theta - \phi)}{\sin 2\phi}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

to which may be given the alternative form

$$\cot 2\phi = \frac{\frac{A}{B} + \cos 2\theta}{\sin 2\theta}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this latter ϕ may be reckoned by the aid of trigonometrical tables, A, B, and θ being all given. Angle ϕ being thus found, it can be used to calculate the maximum and minimum values, namely the two sums previously expressed. The cylindrical lens representing the maximum sum being set at angle ϕ with the original direction of A, and the cylindrical lens representing the minimum sum being set at $90° - \phi$, they will, thus crossed at right-angles to one another, together act as the optical equivalent of the two obliquely-crossed cylinders.

These two rectangularly-crossed cylindrical lenses may again be resolved into the combination of (1) a cylindrical lens, whose axis is along the axis just found for the maximum lens, and of power C dioptries equal to the difference between the maximum and minimum cylindrical powers, and (2) a spherical lens whose power D is that of the minimum. Hence we shall have

$$C=A\cos^2\phi+B\cos^2(\theta-\phi)-A\sin^2\phi-B\sin^2(\theta-\phi);$$

$$C=A\cos 2\phi+B\cos 2(\theta-\phi), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$D=A\sin^2\phi+B\sin^2(\theta-\phi). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

4. The solution thus found is capable of further simplification.

Dividing equation (3) by A, we have:

$$\frac{C}{A}=\cos 2\phi+\frac{B}{A}\cos 2(\theta-\phi).$$

From equation (1) we have

$$\frac{B}{A}=\frac{\sin 2\phi}{\sin 2(\theta-\phi)}.$$

Substituting this in the preceding gives us:

$$\frac{C}{A}=\cos 2\phi+\frac{\sin 2\phi \,.\, \cos 2(\theta-\phi)}{\sin 2(\theta-\phi)},$$

$$\frac{C}{A}=\frac{\sin 2\theta}{\sin 2(\theta-\phi)}.$$

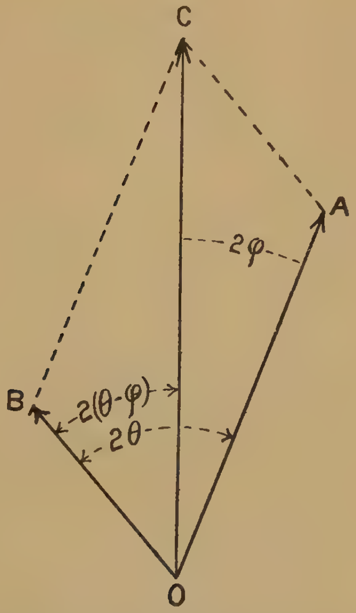
From this immediately follows the relation:

$$\frac{A}{\sin 2(\theta-\phi)}=\frac{B}{\sin 2\phi}=\frac{C}{\sin 2\theta}. \quad . \quad . \quad . \quad (5)$$

This at once suggests that the three magnitudes A, B, and C can be represented by the three sides of a triangle whose respectively-subtended angles are $2(\theta-\phi)$, 2ϕ, and 2θ. Or $2(\theta-\phi)$, 2ϕ, and $\pi-2\theta$. In short, the two given cylindrical components A and B may be compounded to find their cylindrical resultant C by means of a parallelogram *in which, however, the angle between* A *and* B *is drawn as double the actual angle between the axes of the two given components.*

Hence we obtain the graphic construction of fig. 4. Draw the lines O A, O B to represent, in magnitude only, the powers of the two given cylindrical lenses, and make the angle A O B between them *double* the given angle θ. For positive (*i. e.* convergent) cylindrical lenses these directions may be reckoned outwards from the origin, as shown by the arrow heads. For negative (*i. e.* divergent) cylindrical lenses the directions must be reckoned inwards. Compounding OA and OB in the ordinary way, we obtain the resultant OC which represents in magnitude (and in sign) the resultant cylindrical part of the desired equivalent combination; but the angle AOC will be *double* of the angle that the axis of the resultant cylindrical lens will make with the axis of A.

Fig. 4.



It will then be evident that the value of C is at once calculable directly from A, B, and θ by the equation

$$C^2 = A^2 + B^2 + 2AB\cos 2\theta. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Having obtained C, the angle ϕ can be most easily calculated by the relation

$$\sin 2\phi = \frac{B}{C}\sin 2\theta. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It only remains to find the corresponding expression for the power D of the spherical part of the equivalent combination.

Dividing equation (4) by A we have

$$\frac{D}{A} = \sin^2\phi + \frac{B}{A}\sin^2(\theta-\phi).$$

$$= \frac{1}{2}\left\{\frac{\sin 2(\theta-\phi)+\sin 2\phi-\sin 2\theta}{\sin 2(\theta-\phi)}\right\}$$

$$= \frac{1}{2}\left\{1+\frac{B}{A}-\frac{C}{A}\right\}$$

$$= \frac{1}{2}\,\frac{A+B-C}{A},$$

whence

$$D = \frac{A+B-C}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This last result might also have been obtained by remembering that the maximum power being C + D and the minimum power being D (at right angles), the sum of these, namely C + 2D, will be equal to A + B, whatever the angle between the latter.

An example of the use of the three working formulæ (6), (7), and (8) will suffice.

To find the equivalent sphero-cylindrical combination for the following obliquely-crossed cylindrical lenses :—

+ 3·5 cyl. ax. 20° ○ + 2·5 cyl. ax. 35°.

Here
$A = 3{\cdot}5$ dioptries,
$B = 2{\cdot}5$ dioptries,
$\theta = 15°$,
$\cos 2\theta = 0{\cdot}866$,
$\sin 2\theta = 0{\cdot}5$.

By equation (6)

$$C^2 = 12{\cdot}25 + 6{\cdot}25 + (17{\cdot}5 \times 0{\cdot}866)$$
$$= 33{\cdot}65,$$

whence $C = +5{\cdot}8$ dioptries, approximately.

By equation (8)

$$D = \frac{3{\cdot}5 + 2{\cdot}5 - 5{\cdot}8}{2},$$

$$D = +0{\cdot}1 \text{ dioptries (spherical).}$$

By equation (7)

$$\begin{aligned} \sin 2\phi &= \frac{2{\cdot}5}{5{\cdot}8} \times 0{\cdot}5 \\ &= 0{\cdot}215, \\ \phi &= \tfrac{1}{2} \sin^{-1}(0{\cdot}215) \\ &= 6^\circ\, 13', \text{ approximately, beyond the position of A.} \end{aligned}$$

Hence the equivalent combination would be

+ 0·1 sph. ◯ + 5·8 cyl. ax. 26° 13′.

5. The circumstance that the cylindrical part of the resultant of two crossed cylindrical lenses varies from maximum to minimum when the angle between the axes of the two lenses is varied from 0° to 90°, suggests a solution to the practical problem how to make a cylindrical lens of variable cylindricity. If two equal positive cylindrical lenses are used, the value of the cylindrical part of their resultant varies from their sum, when the angle $\theta = 0^\circ$, to zero when the angle $\theta = 90^\circ$. But while the cylindrical part thus diminishes, in proportion to the square of the cosine of the angle between them, the spherical part of the resultant increases in the proportion of the square of the sine of the same angle. One never obtains a simple cylindrical lens, except in the case of the coincidence of the axes. Similarly if two equal negative cylindrical lenses are used, the resultant consists of a negative cylindrical part and a negative spherical part, the one decreasing, the other increasing when the angle θ is increased from 0° to 90°.

Ophthalmists are acquainted with a combination (known as Stokes's lens) consisting of two cylindrical lenses of equal but opposite powers (one a convex, the other an equal concave), arranged to be rotated to various angles of obliquity across one another. When their axes are in coincidence, or $\theta = 0^\circ$, they neutralize one another completely. When crossed at right-angles their resultant cylindricity is a maximum but is mixed in sign. Suppose their respective powers were +2 dioptries and −2 dioptries; they will when crossed not act as either a +4 dioptrie cylinder, or as a −4 dioptrie cylinder, but can be made to act as such by adding at choice either a +2 dioptrie spherical lens or a −2 dioptrie spherical lens, to neutralize the refractive effects in one or other of the meridians. When crossed at intermediate angles the spherical lens required to neutralize, and so produce the effect of a simple cylinder, would be of some intermediate power. This is a slight inconvenience; but a more serious one exists in the circumstance that in rotating one about the other the axis of the resultant cylindrical effect takes a varying obliquity. This objection is not removed by rotating the two lenses in opposite directions simultaneously.

A more convenient combination to give varying degrees of cylindricity is the following:—Let two lenses be ground, each being a mixed equi-cylinder consisting of a concave and convex ground at right-angles to one another on the opposite faces of the glass. Two such mixed cylinders, if rotated with equal motion in opposite directions, will give a varying cylindricity of fixed direction in space. With the axes of +cylindricity coincident they give the maximum; but when each is rotated to 45°, one to the right, the other to the left, their resultant is zero. In intermediate positions the value of the resultant varies according to the square of the cosine of double the angle through which either has been moved (*i.e.* to the square of the cosine of the angle between their axes), but it remains fixed in direction. When each is rotated beyond 45° they begin again to act as a cylindrical lens, but with the resultant axis of cylindricity negative in the fixed direction in which formerly it was positive. An instrument thus constructed* may be graduated so as to be direct-reading.

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* This instrument is called an *Astigmometer*.

VI. *On some Improved Formulæ and Methods connected with Lenses.*

By THOMAS H. BLAKESLEY[*].

IN a paper read before the Physical Society on June 11th, 1897[†], I pointed out the connexion between the distance of an object from the first principal focus of a lens and the relation of its linear magnitude with that of the image produced: viz., that every change in that distance by the amount of the focal length of the lens produced a unit of change in the relation of these magnitudes; and I described methods by means of which the focal length might be very accurately determined upon these grounds.

I also explained how the position of the two principal foci might be accurately determined by placing the lens upon a plane mirror and finding the spot at which if an object be placed its image inverted will coincide with it.

The rules given apply equally well to combinations of coaxial lenses as to single lenses.

Hence all focussing properties of lens-systems are really determined when the three following matters are known:—

(1) The focal length with proper sign.
(2) The position of the first principal focus.
(3) The position of the second principal focus.

The *first* principal focus is defined as the point such that if a beam of light *before* impact on the lens-system is diverging from it or converging to it, then *after* passage through the system the beam will consist of parallel rays.

The *second* principal focus is the point such that if *before* impact the beam is one of parallel rays, *after* passage it will consist of rays either diverging from or converging to that point.

In the present communication I wish to point out the rules by means of which, when these elements are known for any two systems, the elements for the combination of the two systems are readily obtained.

Each lens of course carries its own system of points with it, but an independent variable is necessarily introduced in combining systems at different distances.

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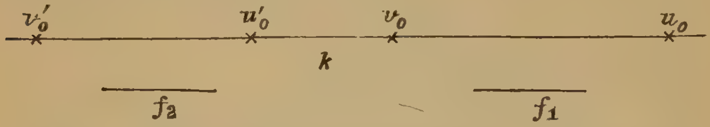
[*] Read December 8, 1899.

[†] Proc. Phys. Soc. vol. xv. p. 178.

The simplest magnitude will be found to be the distance between the second principal focus of the first system and the first principal focus of the second system, which I call k, and which has a positive value in the direction of the propagation of light.

Let u_0, v_0 be the positions of the principal foci of the first system, and u_0', v_0' those of the second system, light being supposed to come from the right.



Let f_1, f_2 be the two focal lengths, and the length from v_0 to u_0' be k.

Then the following rules fix the elements of the whole united system.

The new first principal focus is distant from u_0 towards the right hand $\frac{f_1^2}{k}$.

The new second principal focus is distant from v_0 towards the left hand $\frac{f_2^2}{k}$.

The new focal length is $\frac{f_1 f_2}{k}$.

These rules are virtually equivalent to the following statements:—

The new first principal focus is conjugate by the first system with the first principal focus of the second system.

The new second principal focus is conjugate by the second system with the second principal focus of the first system.

The points u_0, v_0' are conjugate with one another. The travel of the principal focus from u_0 to its final position being easily and accurately determinable by experiment, and having for its theoretical value $\frac{f_1^2}{k}$, it may be employed in a variety of practical ways.

The following example may illustrate how it may be used to find the focal length of a lens in the absence of a magnification apparatus.

The tubes of a telescope retaining the object-glass, but otherwise free from lenses, are placed vertically with the object-glass downwards upon a plane mirror. Crossed silk fibres are stretched across the open end, and the tubes are adjusted till the image of these fibres is in the same horizontal plane as the fibres themselves. The length of the tubes is then found to be 25·95 cms. An achromatic telescope object-glass, whose principal foci are known to be 21·12 and 19·92 from the convex and plane sides respectively, is placed upon the upper end of the telescope-tube before mentioned, the plane side being downwards. A minute triangle of white paper (about 3 sq. mm. in area) is placed in the centre of the upper or convex side, and the tubes of the telescope, still standing on the plane mirror, are manœuvred until the image of this paper coincides with itself. The length is then found to be 25·15 cm. The focal length of this lens can then be determined as follows:—

The principal focus of the lower lens is above the lower surface of the upper lens by the amount of the shortening of the tubes, *i. e.* $\overline{25·95-25·15}$, or ·80. But the position of the second principal focus of the upper lens is 19·92 below this face. Therefore the value of k is $-(19·92+·80)=-20·72$, the negative value being the result of overlap in regard to the two systems.

But the amount by which the outer principal focus moves upwards is $-21·12$.

Hence
$$\frac{f_1^2}{-20·72}=-21·12.$$

Hence $f_1=-20·92$, the negative sign being of course chosen.

Again, if a convex lens, whether achromatic or not, is laid upon a plane mirror, its convex side downwards, a few drops of any refracting liquid being placed between the two, the principal focus will travel a distance depending on the index of refraction of the liquid. Care must be taken that the combination is convex in character.

If r is the radius of the face common to the lens and the liquid and μ is the index of refraction of the liquid, the liquid lens will have for focal length $\frac{r}{\mu-1}$, and its first principal focus will be situated at $\frac{r}{\mu-1}$ below the plane mirror. If v_0 be taken as the distance from the wetted surface of the lens of its own second principal focus, the k of this problem is clearly $\left\{\frac{r}{\mu-1}-v_0\right\}$.

Hence if f be the focal length of the lens, and c be the travel of the first principal focus due to the insertion of the liquid,

$$\frac{f^2}{\frac{r}{\mu-1}-v_0}=c,$$

or

$$\frac{1}{r}\left(\frac{f^2}{c}+v_0\right)=\frac{1}{\mu-1}.$$

If the lens constants are thoroughly known, we have an equation of the form

$$\frac{1}{\mu-1}=\frac{\text{A}}{c}+\text{B},$$

where A and B are both constants.

In practice it would be possible to determine A and B by observing the values of c in the cases of two liquids whose indices have been determined in other ways; but it is not necessary to take this course where a single lens is employed, because in that case the radius r can be expressed in terms of the focal length, the distances u_0 and v_0 of the principal foci from the anterior and posterior surfaces of the lens, and d the thickness of the lens, the latter being easily measured by calipers. The formula for $\frac{1}{r}$ then is

$$\frac{u_0+f}{f^2-u_0v_0+df},$$

which can be inserted in the above equation.

Or if a compound lens is employed, the value of r may be determined by a spherometer; but this instrument does not furnish the most accurate means of calculating such radii. This point will receive attention below.

A telescope is an arrangement of coaxial lenses, some forming what is called the object-glass, others the eyepiece. Each of these portions may be far from simple, but each must have its own focal length and pair of principal foci. When the second principal focus of the object-glass coincides with the first principal focus of the eyepiece, the focal length of the combination is infinite, for the k of this problem is equal to zero. This is often considered to be the position of adjustment for viewing distant objects; and in fact a telescope will always have a very long focal length though the actual value will differ with different eyes. Now if a telescope is in this condition of adjustment, having an infinite focal length, we may divide the system anywhere we please, and call one part the object-glass and the other the eyepiece. All that is necessary is that the dividing surface shall be a plane at right angles to the common axis, or a sphere having its centre on the common axis. The division itself may even take place through one of the lenses.

The two portions of the system thus formed will have the following properties.

The second principal focus of one of them will always coincide with the first principal focus of the other.

The ratio of the two focal lengths will always have the same value, the magnifying-power of the whole, wherever the division is made.

When, for the purposes of celestial photography, a telescope has a camera attached at the eye-end, the question arises how far the eyepiece must be racked out in order to obtain an image on the plate.

If the optical properties of the eyepiece are known, *i. e.* its focal length and the positions of its principal foci, then of course the distance of the camera-plate from the second principal focus is known. But the camera-plate must be in the second principal focus of the whole system. Hence the distance from the second principal focus of the eyepiece to the plate must be the travel of the principal focus due to the application of the object-glass, *i. e.*

$$\frac{f^2}{c} = k,$$

where f is the focal length of the eyepiece, c is the distance of the photographic plate from the second principal focus of the eyepiece, and k is the amount of racking out required from the position in which the focal length of the telescope is infinite.

If we have a lens system, and coaxial with it a mirror, either plane or spherical, and light is passed first through the lens in a direction towards the mirror, and after reflexion at the mirror, back through the lens in the reverse direction, the combination forms a virtual mirror to which the following very simple rules apply:—

> The virtual mirror's surface is conjugate with the real mirror's surface by the lens.
>
> The virtual mirror's centre of curvature is conjugate with the real mirror's centre of curvature by the lens.

These rules enable one at once to determine the general facts of the image-formation in any given case.

If the virtual mirror is a plane one, its radius of curvature is infinite, and either its surface or its centre of curvature must be at infinity, while the other must be at a finite distance.

Hence to form a virtual plane mirror either the surface or the centre of the real mirror must be in the second principal focus of the lens.

If the surface of the mirror makes this coincidence, the surface of the plane virtual mirror will be at infinity; but its centre is not so, and may be easily found experimentally, as the place where an object coincides with an *inverted* image of itself.

If the centre of curvature of the mirror coincides with the second principal focus of the lens, the centre of the curvature of the virtual plane mirror is at infinity; but the plane itself will not be so, and its position may be easily found experimentally as the place where an object coincides with an *erect* image of itself.

Such virtual mirrors, whether plane or not, giving erect images, are of course often formed in front of the lens; and in such cases there is not the smallest difficulty in passing an object "through the looking-glass."

The rules given above for the position of the centre of curvature and surface of the virtual mirror are equivalent to the two following mathematical formulæ :—

The surface of the virtual mirror is situated at a distance from the first principal focus of the lens equal to $\frac{f^2}{k+\frac{r}{2}}$ in a direction contrary to that in which the light is going *before* reflexion; and the centre of curvature of the virtual mirror is situated at a distance from the same point equal to $\frac{f^2}{k-\frac{r}{2}}$ measured positively in the same direction.

In these formulæ f is the focal length of the lens; r is the radius of curvature of the mirror (positive if concave); k is the distance from the second principal focus of the lens to the principal focus of the mirror, measured positively in the direction in which light is proceeding before reflexion.

Now suppose that the mirror coincides in curvature and position with the second face of the lens. This will be the case if either that face is silvered or placed in a pool of mercury.

The position of the centre of curvature of the virtual mirror can be found in the usual way, by coincidence with inversion of the image and object. Let it be distant c from the original first principal focus of the lens, positively measured in the direction opposite to the light before reflexion.

Then by the above formula

$$c=\frac{f^2}{k-\frac{r}{2}};$$

But if v_0 be the distance of the second principal focus of the lens from the second surface, the value of k will be

$$-\left\{v_0+\frac{r}{2}\right\}.$$

Hence $$c=-\frac{f^2}{v_0+r} \text{ or } r=-\frac{f^2}{c}-v_0;$$

all the symbols on the right-hand of this last equation are known.

This affords a very convenient way of practically measuring the radius of curvature of the face of a lens, as a pool of mercury is an easy way of producing the conditions.

I have mentioned above in dealing with the index of refraction of a liquid that a knowledge of this value is important; and this optical method is in my opinion far superior to that of the spherometer in making the determination.

Those who may have followed the above remarks with care will see that I strongly advocate those optical methods of measurement which depend upon making a coincidence between the position of an object and that of its image. These coincidences may be determined with very great precision by any one accustomed to observation; and the apparatus required, though it may be made as elaborate as any others, need be no more than the simplest. A small optical bank about five inches long, a holder to slide up and down and to carry a sharply-pointed piece of white paper, four square inches of good plane mirror, a hand-lens of about 2 inches focal length to determine coincidences, and a rule and calipers to measure distances, are really all that is necessary to make determinations of an accuracy far surpassing that in vogue at present.

I have examined a lantern-projector which professed to have a focal length of 6 inches (=15·24 cm.). It actually possesses one of 17·81 cm.

A microscope objective whose nominal value was $1\frac{1}{2}$ inch, made by the most eminent optician in London, was measured directly, and indirectly by taking its two component lenses separately and measuring their focal lengths and the overlap of their principal foci.

$$\left.\begin{array}{lr}\text{The first method gave} & 1{\cdot}347 \\ \text{,, second ,,} & 1{\cdot}355\end{array}\right\}\text{ inches focal length.}$$

The nominal value was therefore certainly in error by as much as 10 per cent.

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VII. *Some Developments in the Use of Price's Guard-Wire in Insulation Tests.* *By* Prof. W. E. Ayrton, *F.R.S.*, *and* T. Mather *.

Everyone who has to test very high resistances, such as those of short lengths of cable and of good joints in insulated wires, cannot fail to appreciate the immense advantage of using Price's "Guard-Wire" † in eliminating errors due to surface leakages. Continued experience confirms the opinion expressed by one of us in the discussion on Mr. Appleyard's paper in 1896; and in our third paper on Galvanometers, read before the Physical Society in May 1898 ‡, we showed how the principle could be applied to galvanometers, shunt-boxes, &c.

For tests made by the "direct deflexion" method the "guard-wire" properly applied affords complete protection against surface leakage where the ends of the cable tested are near the galvanometer, so that it is possible to have the wire connecting the conductor of the cable with the galvanometer terminal "air insulated." A difficulty, however, arises when the ends of the cable are at a considerable distance from the testing instrument; this may render "air insulation" of the lead impossible, and so the leakage from the lead must be measured and allowed for. As this "lead leakage" may be as large as or larger than that through the mass of the insulation under test, the convenience and accuracy of the measurement are somewhat impaired. It therefore occurred to us that a guard-wire applied to the lead along its entire length would prove of great value in cases such as the one under consideration. The most effective as well as the simplest way of doing this is to use a concentric wire to connect the cable and galvanometer, the inner of the concentric being used as the "lead," and the outer as the "guard-wire."

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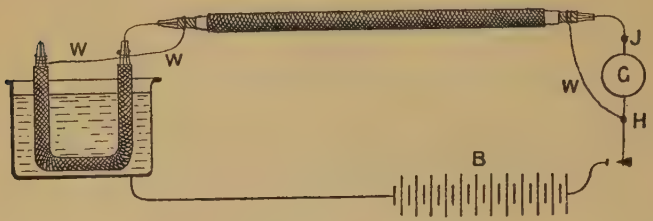
* Read January 26, 1900.

† Electrical Review, vol. xxxvii. p. 702 (1895). See also Appleyard on "Dielectrics," Phil. Mag. xlii. p. 148 (1896); Proc. Phys. Soc. vol. xiv. pp. 257, 264.

‡ See Phil. Mag. Oct. 1898, p. 368, and Proc. Phys. Soc. vol. xvi. p. 191.

Fig. 1.

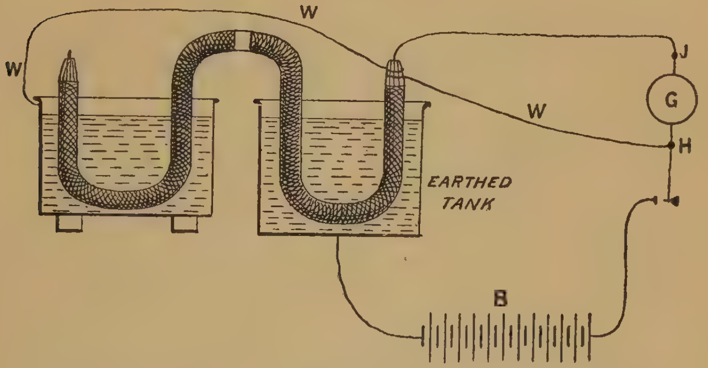


The arrangement is shown symbolically in the sketch above. It will be readily understood that so long as the insulation resistance of the outer of the concentric is high compared with the internal resistance of the battery the method indicated gives complete protection against lead leakage and surface leakage, even if the concentric be laid along the ground for a considerable distance.

Other instances in which special applications of the guard-wire principle have been found convenient have arisen in cases where it has been necessary to determine whether a defective piece of cable was bad throughout, or bad owing to one or more isolated faults. When two tanks are available and one of them can be moderately well insulated from earth, the method of procedure is to coil about half the cable in each tank, remove the metal sheathing (if any) from a short length, say one inch, of the cable between the two tanks, and connect the guard-wire with the insulated tank as well as wrap it round the insulating covering near the extremity of the cable, as shown in fig. 2. In the case of braided and other unsheathed cables, the covering of the portion between the two tanks need not be removed. An insulation test applied under the above conditions gives the resistance of the part of the cable in the earthed tank, and a comparison of this with the insulation resistance of the whole will show whether one half is worse than the other half. By repeating this test with say one quarter of the cable in the earthed tank, and the remainder in the other tank, the question of local *v.* general leakage may be decided.

Instead of two tanks, two drums, one of which can be fairly well insulated, might be employed, or one drum and one tank used, for we find that after the braiding of a cable has been thoroughly wetted it acts as a fair conductor for several hours, even on a dry day. It is therefore not essential to have the part tested completely immersed, although of course immersion is conducive to constancy of temperature. Sufficient connexion with the wet braiding can be made by wrapping bare wire round it. If the cable be long this may be done at several places along its length.

Fig. 2.



By employing the two drums above mentioned faults in braided and other unsheathed cables can be readily localized, without in any way injuring the cable. After connecting the guard-wire with the insulated drum the wetted cable is wound from the earthed drum to the insulated one, the galvanometer being connected with the inner conductor during the process. When the fault passes to the insulated drum a sudden diminution of deflexion occurs.

In some cases we have only used one tank (the earthed one in fig. 2) in testing part of a coil of cable, the remainder being first wetted and hung up on a wooden beam supported between two tables. By inserting metal sheets connected with the guard-wire between the beam and the tables, errors which might otherwise arise from surface leakage are eliminated.

The guard-wire properly applied gives complete protection against surface-leakage errors when the tests are made by the "direct deflexion" method, but in the "loss of charge" test it is desirable to make measurements both with and without a guard-wire. Unless this be done one cannot be sure that surface leakage is not influencing the results obtained.

A little consideration will show that if any surface leakage exists a guard-wire will tend to keep up the potential of the inner conductor during the period of "insulation," and therefore cause the insulation resistance to appear *greater* than its true value; whereas if no guard-wire be used surface leakage will facilitate discharge and cause the insulation resistance to appear *less* than its true value. If, however, the two tests give about the same result (care having been taken to properly discharge the cable between them) we have proof that the effect of surface leakage is inappreciable. It is frequently more expeditious to make the two tests above mentioned than to clean and coat the ends with paraffin-wax in such a way as to make one feel confident that no surface leakage exists.

In making the guard-wire measurements it is desirable to put the guard as near the braiding or sheathing as practicable, consistent with keeping the resistance between the guard-wire and the sheathing high compared with that of the battery. By so doing any error due to the guard-wire is lessened, for the path over which surface leakage can occur is made as long as possible and nearly equal to that over which leakage takes place when no guard-wire is used. An approximate correction is then possible, even when the two tests with and without the guard-wire do not give the same result.

Suppose, for example, the swing of the galvanometer-needle on the first charge is s_1 divisions, and s_2, s_3 were the swings on "recharge" after the same period of "insulation" with and without guard-wire respectively, then the value of the recharge swing, if no surface leakage existed, would be given by the expression

$$s = \frac{s_2}{1 - \frac{s_3 - s_2}{2s_1}} \text{ approximately.}$$

The preceding formula is generally sufficiently accurate for practical purposes, but it is possible to obtain *absolute* accuracy in the use of the guard-wire with the "loss of charge" insulation test in the following way. Instead of maintaining the potential of the guard-wire constant, while that of the insulated conductor is steadily falling, cause the potential of the guard-wire to fall at the same rate as that of the insulated conductor. Then no electricity can pass between the conductor and the guard-wire, and surface leakage will be absolutely prevented.

A potentiometer and an electrostatic voltmeter can be conveniently employed in carrying out this experiment, and it is interesting to remember that the Thomson and Varley potentiometer was originally devised for the special object of enabling the potential of one conductor to be made to diminish as the potential of another conductor steadily fell by leakage. This was not of course in connexion with the use of Price's ingenious guard-wire, but in the days of the old "divided-ring electrometer," before it was known how to make a quadrant electrometer with the deflexions *directly* proportional to the P.D. to be observed, and when, therefore, a zero method had to be employed in carying out the "loss of charge" insulation test.

DISCUSSION.

Mr. CAMPBELL said that the necessity of having a concentric cable could be obviated by simply hanging the lead from the guard-wire by short lengths of material of fair insulation. The guard-wire must be bared at the points of suspension.

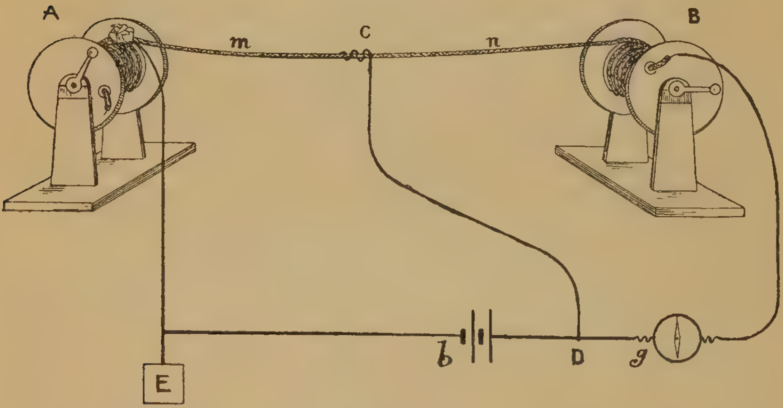
Mr. PRICE expressed his interest in the developments of his principle which had been made by the authors.

VIII. *Fault Tests for Cable Core.*

By Rollo Appleyard.*

The following method of localizing faults has been found especially useful for braided core, and for core protected by ozokerited-tape. It does not require these coverings to be removed or cut. Fig. 1 shows a convenient arrangement of the test. Drums A and B are supported upon ebonite bearings. The electrical connexions are those of the "direct deflexion" method, with the addition of a wire, C D, called the "guard-wire." The guard-wire terminates at C in a rubbing-contact piece, which may be a metallic brush or a wet sponge. The ends of the core are brought out through the flanges of the drums. For the sake of clearness, the ends in fig. 1 are shown connected directly to the testing circuit; in practice each end of the conductor should be connected to the iron axle of its corresponding drum. Contact with the testing-circuit can then be made through the brass bushing of the ebonite bearing of drum B. A wet cloth attached to an an earth-wire, shown on drum A, can be placed either upon A or B. In the case of bare core it is convenient to cover the whole length from A to B with damp cloth.

Fig. 1.



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* Read January 26, 1900.

Faults in core may be (1) single, (2) multiple, or (3) distributed. They may vary in resistance from zero to comparatively high values. It is probable that for each class of fault there is a particular method best suited for determining its position. But whatever the nature of the fault, the guard-wire will be found a most useful aid to localization.

(1) When a single fault of low resistance passes through the contact at C, its presence is indicated by a sudden *fall* in the deflection, for the galvanometer is at that moment automatically short-circuited through the conductor of the cable. Note that the galvanometer is thus completely protected. Simultaneously the battery is connected directly to the fault, and generally burns it out.

(2) A fault thus localized should be removed, by cutting it away from the dielectric, and temporarily repaired. The core can then be carried on through C. If there are several faults, the deflexion will fall as each in succession passes the guard-wire.

(3) In the case of faults distributed along several inches, or even yards, of the core, the bad portion can always be brought to the intermediate stretch from A to B. For this purpose, the earth-cloth should first be laid upon A, and the deflexion noted; it should then be removed to B, and the corresponding deflexion observed. This determines whether the faulty portion is upon A or upon B, and by winding core from the faulty drum to the good drum, in measured lengths, and by comparing corresponding successive pairs of deflexions, the faulty portion passes ultimately from one drum to the other. If the faulty portion is in this way located somewhere along the stretch between C and B, it is clear that by moving the guard-wire from C towards B the deflexion will gradually diminish, for the current through the galvanometer is thereby more and more shunted. If the fault is uniformly distributed, the fall of deflexion is approximately proportional to the distance thus traversed by C. The rate at which it falls as C moves towards B can be compared with the rate of falling when good core is substituted for the faulty portion, between C and B.

Appendix.

Qualitative tests are, as a rule, sufficient for localizing faults in such lengths of core as can be handled in this convenient way. Some interest, however, attaches to the quantities involved, especially as the equations happen to be applicable to nearly all cases arising from the use of a guard-wire.

In a paper read before the Physical Society in May 1896,* upon "Dielectrics," certain tests by the "direct deflexion" method were described, in which the "guard-wire," suggested by Mr. W. A. Price, was used to prevent end-leakage. For this purpose the guard-wire was applied so as to intercept the path of leakage at the "end" of the core. It was therefore placed at a point about halfway along the cleaned "end," thus leaving about three inches of cleaned dielectric on each side of it. In the present use of the guard-wire for localizing faults, it may be supposed removed from the "ends" and applied to the braiding at some point of the stretch of core intermediate between the drums, as at C in fig. 1. The core may be braided or taped, and it may be wet, without prejudice to this method of localizing faults. Let the total surface-resistance between A and B be $m+n$ ohms, intercepted by the guard-wire at C between m and n. The "ends" need not be cleaned; and we may suppose the core, including that on the drums, to be thoroughly wet. The resistance m, in effect, shunts the battery; similarly n shunts the galvanometer. Also let r be the ordinary "dielectric resistance" of the total length of core when there is no fault; f the resistance of the fault; b the battery resistance; g the resistance of the galvanometer; and E the E.M.F. of the battery. Then, so far as it is permissible to apply Kirchhoff's laws to such "resistances," † the current G through the galvanometer is given by:

$$G = \frac{E}{(r+g+b) + \left[\frac{g}{m}(r+b) + \frac{b}{n}(r+g) + \frac{brg}{mn}\right]}.$$

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* Proc. Phys. Soc. vol xiv. p. 255.

† 'Electrician,' July 24th, 1896, p. 403.

If the fault is on the A side of C, it is necessary to substitute $\frac{mf}{m+f}$ for m. If the fault is on the B side, $\frac{nf}{n+f}$ should be substituted for n. By evaluating the above expression for G, almost any case can be examined, either for the purposes of the present test, or for any application of the guard-wire. The best way to determine the magnitude of possible errors is first to evaluate the quantity included between the square brackets, and then to compare this with $(r+g+b)$.

IX. *The Frequency of Transverse Vibrations of a Stretched Indiarubber Cord.* *By* T. J. Baker, *B.Sc.**

The writer has observed that the pitch of the note produced by twanging an indiarubber band which is stretched over the fingers is influenced but little by the tension, particularly if this is considerable.

The matter appeared worthy of further investigation; and for this purpose a short piece of indiarubber cord, of square section, was attached at one end to the middle of a tambourine-diaphragm, while the other end was bound to a piece of twine which passed over a pulley-wheel and supported a weighed scale-pan.

After placing a weight in the pan, the rubber was allowed to stretch for some minutes, and then the end nearest the pan was firmly clamped. The intensity of the note produced by transverse vibrations of the cord was rendered sufficiently great by the tambourine to permit a determination of pitch by comparison with a sonometer and tuning-fork.

The sectional area of the cord under the various tensions employed was determined by measurements of its two diameters at three different points in its length.

For this purpose a micrometer-gauge reading to ·001 cm. was employed. The observations were continued until the cord broke. This happened when its length had increased six-fold. The 38 sets of values thus obtained were plotted on squared paper, and three curves were drawn showing the relation between—

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* Read January 26, 1900. (Communicated by Prof. Poynting.)

(i.) Length and tension.
(ii.) Length and sectional area.
(iii.) Length and frequency.

The smoothing-out of slight experimental irregularities which these curves effect was found of advantage in the calculations hereafter referred to.

Inspection of the curve connecting length with tension reveals that the relation is strictly linear between those points at which the length of the cord becomes respectively 2½ and 5 times its natural length.

Untrustworthy readings were obtained with further stretching because an increase of tension did not produce its full effect until a very considerable time had elapsed. With the smaller stretchings this difficulty was not encountered.

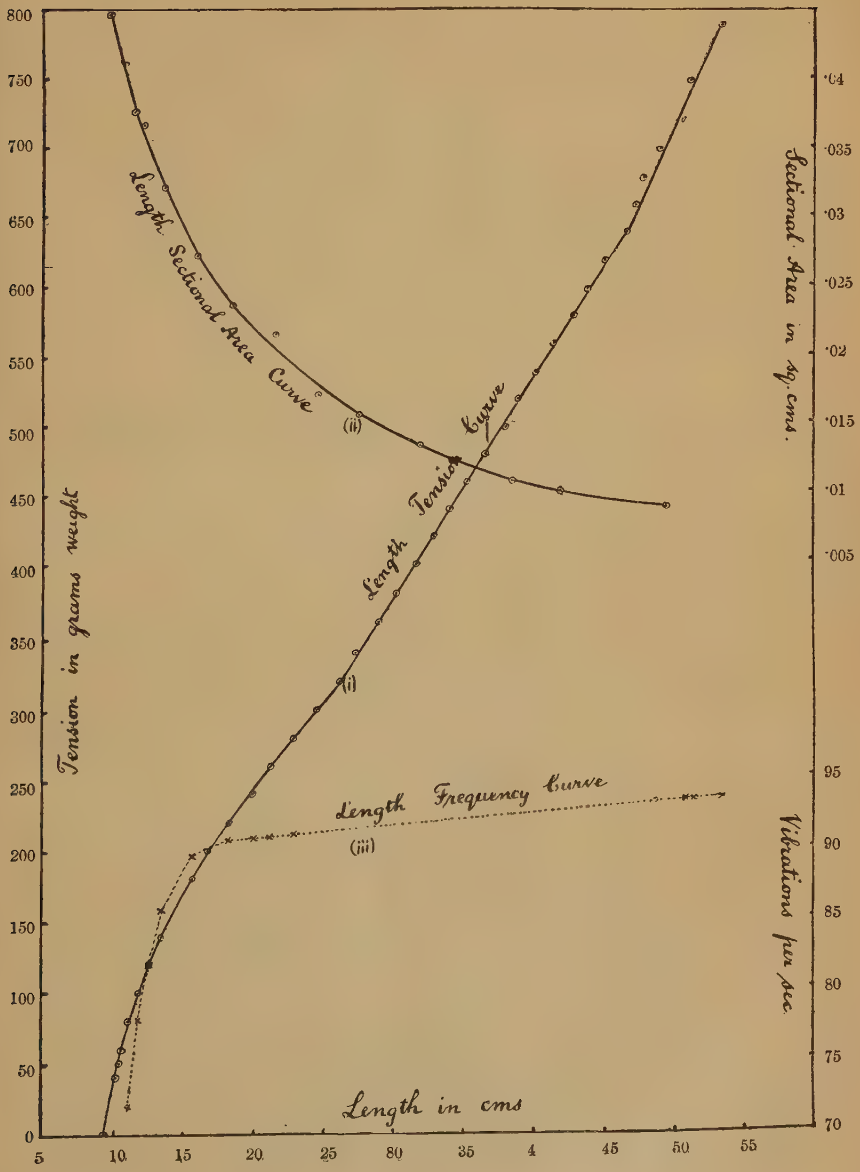
The curve connecting length with frequency shows that while the cord was doubling its natural length the pitch of its note was rising rapidly; but that further extension was practically without effect.

When the cord had doubled its natural length, its frequency of vibration was 91; and when its original length had been sextupled the frequency was not more than 94.

The discussion which follows relates to the conditions prevailing during the period in which length and tension are connected linearly.

Since the observations show that equal increments of tension (between the limits above mentioned) produce equal extensions; and at the same time the sectional area is diminishing, it appears that the value of Young's modulus must increase with increasing extension.

Experiments have been made on this point by Villari (Pogg. *Ann.* cxliii.), by Röntgen (*ibid.* clix.), and by Mallock (Proc. Roy. Soc. 1889); but beyond ascertaining that Young's modulus increases rapidly with increase of extension no definite relations appear to have been discovered.


Length Sectional Area Curve
(ii)
Length Tension Curve
(i)
Length Frequency Curve
(iii)
Tension in grams weight
Length in cms
Sectional Area in sq. cms.
Vibrations per sec.
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
5
10
15
20
25
80
35
4
45
50
55
·04
·035
·03
·025
·02
·015
·01
·005
95
90
85
80
75
70

The values of the modulus for the cord used in these experiments were therefore calculated by the use of curves (i.) and (ii.).

In each case an extension of 1 cm. was chosen, and the increase of tension required to produce this was 16 grams weight.

The mean value of the sectional areas before and after each increase of tension was used in the calculation; and for this purpose curve (iii.) was employed.

When the results are tabulated, it becomes apparent that *Young's modulus is proportional to the square of the stretched length of the cord.*

The last column in the table exhibits this relation.

TABLE showing Relation between the stretched Length of an Indiarubber Cord and the corresponding Value of Young's Modulus.

Natural dimensions of the cord 9·3 cm. × ·22 cm. × ·221 cm.
Frequency of the stretched cord = 93.

Original Length in cms.	Final Length in cms. (L).	Sectional Area in sq. cms.	Increment of Tension in grams weight.	Young's Modulus. (Y).	$\frac{Y}{L^2}$.
26	27	·0159	16	26163	35·9
28	29	·0148	16	30270	36·0
30	31	·0138	16	34782	36·2
32	33	·0128	16	40000	36·7
34	35	·0121	16	44958	36·7
36	37	·0112	16	51200	37·3
38	39	·01057	16	57508	37·8
40	41	·0101	16	63366	37·6
42	43	·0097	16	69278	37·4
44	45	·0094	16	74734	36·9
45	46	·00927	16	78431	37·0

If this relation is borne in mind, it can be shown that the frequency of a greatly stretched rubber cord will increase very slowly indeed with increase of tension.

Let $T =$ tension.
$l =$ natural length of the cord.
$L =$ stretched " "
$m =$ mass of unit length of cord.
$w =$ mass of cord.
$\rho =$ density of the rubber.
$s =$ sectional area of the cord.
$Y =$ Young's modulus.

Then between the limits previously specified,

$$\frac{dT}{s} = Y \frac{dL}{L}.$$

But $$\rho s L = w;$$

$$\therefore \quad \rho \frac{dT}{w} = Y \frac{dL}{L^2}.$$

Now since it has been shown that

$$Y = kL^2;$$

$$\therefore \quad \rho \frac{dT}{w} = k.dL\,;$$

$$\therefore \quad \frac{\rho}{w} T = kL + C^*.$$

Put $T=0$ when $L=l$,

$$\frac{\rho}{w} T = k(L-l).$$

But $$w = Lm,$$

$$\therefore \quad \frac{\rho T}{Lm} = k(L-l);$$

and

$$\frac{1}{L^2} \cdot \frac{T}{m} = \frac{k}{\rho}\left(\frac{L-l}{L}\right).$$

Also for a vibrating string

$$n = \frac{1}{2L}\sqrt{\frac{T}{m}};$$

$$\therefore n \propto \sqrt{\frac{L-l}{L}}.$$

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* This assumes ρ constant. Villari found the density of rubber which was stretched four times its natural length to be ·966 times its natural density.

The value of this expression increases very slowly with increase of L if the latter is several times l. This appears to be the explanation of the remarkable constancy in pitch of the note given by the vibration of a rubber cord under increasing tension [*].

King Edward's School, Birmingham.

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X. *The Relative Rates of Effusion of Argon, Helium, and some other Gases.* *By* F. G. Donnan, *M.A., Ph.D., Junior Fellow, Royal University of Ireland* [†].

Introduction.

While investigating argon and helium, Prof. Ramsay and Dr. Collie [‡] have found that these gases *diffuse* through a porous plug into a vacuum with velocities which are higher, when compared with a standard gas such as oxygen, than those calculated according to the law of the inverse square root of the density. The object of the present investigation is to ascertain the relative rates of flow of these gases through a small hole in a thin-walled partition, *i. e.* their relative rates of *effusion*.

The subject of the efflux of fluids was investigated by D. Bernouilli [§]. Since that time the subject has been investigated both theoretically and experimentally by numerous writers. In the present case we have only to deal with the efflux of gases. So long ago as 1804 Leslie [‖] suggested the determination of relative densities by this means, and in fact described the method which was afterwards worked out by

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[*] Since this was written, the author's attention has been directed to a paper on the same subject by von Lang (Wied. *Ann.* vol. lxviii.). The constancy of pitch is briefly mentioned as due to an observed proportionality between the tension and the stretched length of the rubber cord. The paper deals chiefly with small discrepancies between the frequencies observed and those calculated from Taylor's formula.

[†] Read March 2, 1900.

[‡] Proc. Roy. Soc. vol. lx. p. 206.

[§] *Hydrodynamica*, 1738, Sec. 10, pr. 34, p. 124.

[‖] 'Experimental Inquiry into the Nature and Propagation of Heat,' p. 534.

Bunsen[*]. The subject was taken up by G. G. Schmidt[†] in 1820; and he deduced from his experiments the law of the inverse square root of the density, *i. e.* the law which was rediscovered by Graham. The subject was then treated in a masterly fashion by de Saint-Venant and Wantzel[‡]. They obtained the equation for the adiabatic efflux of an ideal gas on the assumption[§] that the pressure at the *vena contracta* is equal to the external pressure; and they likewise observed that this equation leads to absurd results when the external pressure becomes zero. Their experiments showed the efflux to be independent of the external pressure, when the latter is less than about one-half the pressure in the gas-reservoir; and they suggest empirical formulæ for dealing with this case. About this time occur the classical experimental researches of Graham[‖]. His experiments were conducted with minute holes in very thin-walled partitions; and he coined the word effusion to denote the efflux in this case. It must be observed, however, that so long as the apertures are not comparable with molecular dimensions, the phenomenon of effusion is simply that of efflux on a small scale. The important point is that the diameter of the hole should be sufficiently large, when compared with the thickness of the partition, to render the effects due to viscosity negligibly small. Graham's experiments established the law of the inverse square root of the density[¶]. Hydrogen, however, showed a marked deviation, which was rightly attributed by Graham to the effect of viscosity being more marked in this case owing to the lightness of the gas. The efflux of gases was investigated by Weisbach[**], and by Thomson and Joule[††]; but the theory was not advanced beyond the point to which it been carried by Saint-Venant and Wantzel. In 1886 the adiabatic theory of efflux was subjected to an elaborate experimental investigation by Hirn*, who rediscovered† the phenomenon observed by Saint-Venant and Wantzel, and came to the conclusion that the theory was incorrect. In the same year, however, Hirn's experimental results were very fully recalculated by Hugoniot‡, who showed that they were not in discord with the theory when the latter was extended in some important respects. The experiments of Wilde led Osborne Reynolds§ to reinvestigate the theory, and he arrived, practically simultaneously with Hugoniot, at the same important extension of the theory. Quite recently the efflux of gases has been the subject of an elaborate memoir by Parenty‖, who rejects the formulæ given by the adiabatic theory, and proposes other formulæ in their stead. Finally, the secondary phenomena in the jet have been investigated by E. Mach and Salcher, L. Mach, R. Emden, and others¶.

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[*] *Gasometrische Methoden*, Braunschweig, 1857, p. 128 *et seq.*

[†] Gilb. *Ann.* Bd. lxvi. p. 39 (1820).

[‡] *Journ. de l'Ecole Polyt.* tom. xvi. cah. 27, p. 85 (1839).

[§] Navier, "Mémoires sur l'Écoulement des Fluides Élastiques," tome viii. de *l'Académie des Sciences,* Juin 1829.

[‖] Phil. Trans. iv. p. 573 (1846).

[¶] Many of Graham's results show that the "law" is subject to considerable deviations.

[**] *Experimental Hydraulik,* 1855, p. 184 *et seq.*

[††] Proc. Roy. Soc. 1856, p. 178.

Theory.

Assuming (1) That viscosity effects are eliminated,
(2) That the ideal gas laws hold,
(3) That the outflow is adiabatic,
(4) That the motion is steady,

the theory given by Saint-Venant and Wantzel, and extended by Hugoniot and Osborne Reynolds, leads to the formula:—

$$\text{Mass-efflux} = \mathrm{S}' p_0 \left(\frac{p_1}{p_0}\right)^{\frac{1}{\gamma}} \sqrt{\frac{2\gamma}{\gamma-1}\,\frac{1}{\mathrm{RT}}\left[1-\left(\frac{p_1}{p_0}\right)^{\frac{\gamma-1}{\gamma}}\right]},$$

where S' = area of *vena contracta*,
p_0 = pressure inside gas-reservoir,
p_1 = external pressure,
γ = ratio of two principal specific heats,
T = temperature of quiescent gas in reservoir,

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* *Ann. de Chim. et de Phys.* sér. 6, tom. vii. p. 289 (1886).

† It is remarkable how often this phenomenon has been rediscovered. Thus it was observed by Graham, Hirn, Napier (Engineer, 1867), Wilde (Phil. Mag. 1886).

‡ *C. R.* 1886, *passim*; *Ann. de Chim. et de Phys.* Nov. 1886.

§ Phil. Mag., March 1886.

‖ *Ann. de Chim. et de Phys.* viii. pp. 1–79 (1896), xii. pp. 289–373 (1897).

¶ Wied. *Ann.* lxix. 1, pp. 264–289 (1899), where Emden gives references to the previous literature.

provided the external pressure is greater than a certain fraction of the internal pressure in the gas-reservoir.

I have not carried out experiments under the conditions required by this formula for several reasons:—(1) The formula does not lead to simple comparative results for two gases possessing *different* values for γ. (2) The efflux in this case is slower, and therefore less likely to be adiabatic. (3) The efflux is dependent on the back pressure, which introduces an additional variable factor in comparative experiments. If, however, $p_1 < \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}} p_0$, then the theory leads to the formula

$$\text{Mass-efflux} = \mathrm{S}' \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \sqrt{\gamma p_0 \rho_0},$$

where ρ_0 = density of quiescent gas in reservoir.

Hugoniot's recalculations of Hirn's results show that S′, the area of the vena contracta, must be taken as a function of the pressure, unless the orifice in the thin plate be provided with a conical or conico-cylindrical nozzle. In the following experiments S′ is therefore taken as a function of the pressure; but it is assumed that this function does not vary with the nature of the gas which is effusing.

In the paper referred to above Parenty has succeeded in representing Hirn's results by means of the empirical formula

$$\mathrm{V}_0 = \sqrt{2a} \,.\, m\mathrm{S} \sqrt{\frac{2g}{\rho_0}\left[p_0 - p_1 - \frac{m}{2ap_0}(p_0 - p_1)^2\right]},$$

where S = area of orifice,
m = a coefficient varying with the nature of the orifice or nozzle,
$2a$ = a constant varying with the nature of the gas,
V_0 = volume-efflux.

If we imagine V_0 plotted against p_1 as the latter decreases from $p_1 = p_0$ to $p_1 = 0$ (p_0 remaining constant), it will be observed that V_0 becomes a maximum for $1 - \frac{p_1}{p_0} = \frac{a}{m}$, and that the maximum value is given by

$$(\mathrm{V}_0)_{\text{max.}} = a\mathrm{S}\sqrt{2gm\frac{p_0}{\rho_0}}.$$

This value is independent of p_1. Parenty regards the efflux as "regulating itself" when p_1 falls to the value $\left(1-\frac{a}{m}\right)p_0$, and becoming constant and equal to the above value. The critical value of p_1 on the adiabatic theory is given by

$$1-\frac{p_1}{p_0}=1-\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}.$$

In Parenty's formula the critical value of p_1 corresponds to

$$\left(1-\frac{p_1}{p_0}\right)=\frac{a}{m}.$$

Hence, to make both theories agree in the critical value of p_1, we have

$$a=m\left\{1-\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}\right\}.$$

According to Parenty, therefore, we have, for the volume-efflux in the region where $p_1 <$ the critical value, the formula

$$V_0=mS\left[1-\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}\right]\sqrt{2gm\frac{p_0}{\rho_0}}.$$

It remains now to consider the application of these results to the conditions under which the following experiments were carried out. The first remark to make is that p_0 was not kept constant, but decreased considerably during the course of an experiment. If, however, we neglect acceleration-terms we may consider the equations as giving the *instantaneous* efflux at any moment, and integrate between the limits of pressure corresponding to any actual experiment. Secondly, the dimensions of the apparatus were so chosen that the back-pressure p_1 in the receiver (which was initially vacuous) never attained its critical value, which is about one-half of p_0. Accordingly we have to apply either the equation

$$\text{Mass-efflux}=xS\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{2(\gamma-1)}}\sqrt{\gamma\, p_0\, \rho_0}\quad (\textit{Hugoniot-Reynolds}),$$

or the equation

$$\text{Mass-efflux}=mS\left[1-\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}\right]\sqrt{2gm\, p_0\, \rho_0}\quad (\textit{Parenty}).$$

The progress of the effusion was determined by means of a closed mercury barometer-gauge attached to the reservoir out of which the gas was effusing ; so that the volume of the gas-reservoir was not constant, but a *function* of the pressure p_0 of the gas in the reservoir at any moment. Call this $\phi(p_0)$. Accordingly the mass-efflux is given by

$$-\frac{dM}{dt} = -\frac{1}{RT}(\phi + p_0\phi')\frac{dp_0}{dt}.$$

If we put

$$\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{2(\gamma-1)}}\gamma^{\frac{1}{2}} = f(\gamma),$$

we can also write using the adiabatic theory,

$$-\frac{dM}{dt} = Sf(\gamma)\frac{xp_0}{\sqrt{RT}},$$

where x is a function of p_0. Equating these values and integrating, we obtain for the time t, during which the pressure in the reservoir sinks from p_0' to p_0'', the equation

$$t = \frac{1}{Sf(\gamma)\sqrt{RT}}\int_{p_0''}^{p_0'}\frac{\phi + p_0\phi'}{xp_0}\,dp_0.$$

If now we measure the times t_1 and t_2 for two different gases, in the same apparatus, at the same temperature, and between exactly the same limits of pressure, we obtain the very simple formula

$$\frac{t_1}{t_2} = \frac{f(\gamma_2)}{f(\gamma_1)}\sqrt{\frac{\rho_1}{\rho_2}}.$$

Employing Parenty's elliptical formula, we obtain

$$\frac{t_1}{t_2} = \frac{\phi(\gamma_2)}{\phi(\gamma_1)}\sqrt{\frac{\rho_1}{\rho_2}},$$

where

$$\phi(\gamma) = 1 - \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}.$$

Suppose now that $\gamma_1 = 1{\cdot}408$ and $\gamma_2 = 1{\cdot}67$. Then we obtain

$$\frac{t_1}{t_2} = 1{\cdot}06\sqrt{\frac{\rho_1}{\rho_2}} \quad (\textit{Hugoniot-Reynolds}),$$

$$\frac{t_1}{t_2} = 1{\cdot}084\sqrt{\frac{\rho_1}{\rho_2}} \quad (\textit{Parenty}).$$

These results indicate a marked deviation from the simple "isothermal" formula $\frac{t_1}{t_2} = \sqrt{\frac{\rho_1}{\rho_2}}$ in cases where two gases are compared which possess very different values for γ. It accordingly becomes a matter of great interest to measure the relative effusion-rates of two such gases as argon and oxygen, which approximate very closely in their behaviour at moderate temperatures and pressures to the ideal gas and yet possess very different values of γ. The theory indicates that argon ought to effuse, when compared with oxygen, considerably *faster* than would be calculated from the densities alone.

Method of Measurement and Description of Apparatus.

It will be seen that the theory sketched in the foregoing section only leads to simple comparison-formulæ for the case of effusion in which the back-pressure is small in comparison with the pressure in the gas-reservoir. The following experiments were made with an initial pressure in the gas-reservoir which was about 700 mm. in one series and about 500 mm. in the others, the back-pressure rising from zero to 60 and 47·5 mm. respectively. The principal condition was, however, that the apparatus should be such as to admit of measurements being made with small quantities (20–30 c.c.) of the rarer gases. It was necessary, therefore, to employ very small apertures in order to reduce the unavoidable error in the time-measurement * to a sufficiently small percentage. There was a limit placed to the thickness of the partition, seeing that it had to withstand pressures approaching that of an atmosphere without collapsing, and so the conditions imposed tended rather in the direction of viscosity-effects. As will be seen in the sequel, such effects made themselves apparent. They could doubtless have been avoided by the employment of large quantities of gas and much larger apertures, but that was not possible in the present case. The apparatus employed is shown in the figure: *a* is the gas-reservoir, the gas being introduced through the capillary tubing *b c d* by means of the gassyphon *e*. The pressure was read off in the closed barometer-gauge *f* by means of a mirror-glass scale. The effusion-plug, or partition containing the effusion-aperture, was placed at or near the lower extremity of the glass tube *g* ; *h* represents a ground-glass joint with external mercury seal. During an experiment, the taps *i*, *j*, *k*, and *l* being closed and *m* open, the gas passed from the reservoir *a* into the vacuous receiver *p* through the narrow aperture in the effusion-plug. The tube *n* led to a Töpler pump, which served to evacuate the apparatus and to collect the gas again at the conclusion of an experiment. Both gas-reservoir and receiver were kept at a constant temperature by being immersed in a very large beaker of water. The temperature of the water was maintained uniform and constant by means of a stirrer with horizontal screw-shaped blades driven by a Heinrici hot-air motor and an Ostwald temperature-regulator filled with toluene.

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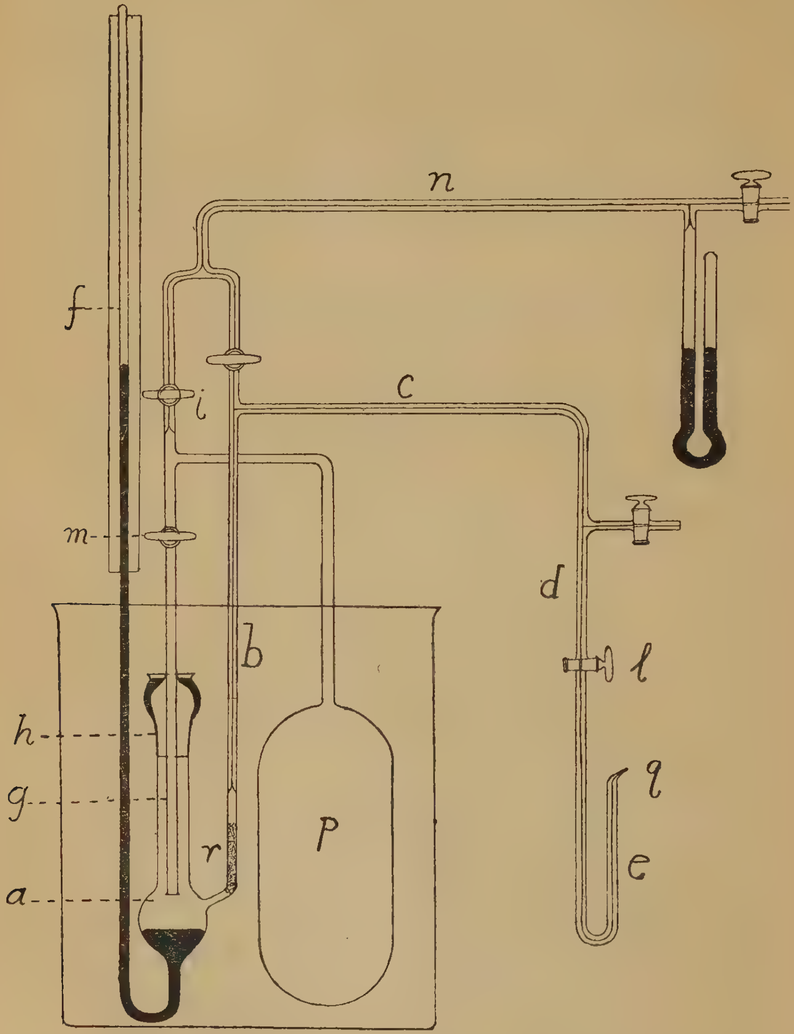
* The time was measured by a stop-watch marking fifths of a second.

In order to make a measurement with the apparatus, the mode of procedure was as follows :—The end *q* of the bent capillary tube was drawn off to a fine point and sealed. The taps *i*, *j*, *l*, and *m* were opened and the apparatus exhausted. These taps were then closed, and the tube containing the gas over mercury brought over the sealed point *q* by raising and lowering the mercury trough. The drawn-out end, which had been previously weakened by a file-scratch, was now broken by pressing the top of the tube against it, and the gas admitted to the reservoir by opening the tap *l*. On its way thither it was filtered through the cotton-wool plug *r*. The gas was allowed to enter until the mercury in the gauge rose to a certain fixed scale-division n_1. It was easy to adjust this accurately, provided the capillary had been drawn out fine enough ; and in any case small inaccuracies in this adjustment are absolutely without effect on the measurements, as is foreseen from the theory and as will be confirmed later on. The tap *l* having been closed, the effusion was started by opening the tap *m* and a stop-watch set in motion as soon as the mercury meniscus sank to a certain scale-division n_2 a little below n_1. A smooth and easy motion of the falling mercury meniscus was secured by having a small quantity of glycerine in the gauge, *i. e.* just sufficient to lubricate the glass wall but not enough to collect over the mercury. The watch was stopped as soon as the meniscus reached a third fixed division, n_3. Proceeding in this way with each of the



gases to be compared, it will be seen that the times of effusion are measured between exactly the same limits of pressure. The pressure in the receiver at the end of the effusion was measured roughly by opening *i* and reading the closed gauge S. In order to make two consecutive measurements, it was only necessary to open *i*, pump out the receiver *p*, close *i*, and readjust the pressure in the reservoir to n_1 by admitting more gas.

Experimental Results.

Besides argon and helium the following gases were investigated :—Hydrogen, oxygen, carbon monoxide, nitrogen, carbon dioxide, and cyanogen. The methods employed in their preparation may be briefly indicated here.

Oxygen.—By heating $KMnO_4$. Dried by P_2O_5.

Hydrogen.—By heating palladium-hydrogen in vacuo. Dried by P_2O_5.

Nitrogen.—Prepared in vacuo from sodium hypobromite solution and ammonium chloride. Passed through powdered NaOH, and dried by P_2O_5.

Carbon monoxide.—Prepared directly over mercury by addition of concentrated formic acid to excess of concentrated sulphuric acid.

Carbon dioxide.—By heating $NaHCO_3$ in vacuo. Dried by $CaCl_2$ and P_2O_5.

Cyanogen.—Prepared by heating $Hg(CN)_2$ in vacuo and dried by P_2O_5. Purified by freezing out in bath of liquid air and pumping off any admixed nitrogen.

The first experiments were made by using very thin-walled glass bulbs in which minute holes had been pierced. This piercing was effected by employing the spark from a Wimshurst machine between terminals of platinum wire. When an aperture of suitable dimensions had been obtained in this way, the stem of the bulb was sealed on close to a capillary tap, and the whole then sealed into the gas-reservoir. Accordingly, in these first measurements, the effusion vessel had a form which was somewhat different to that described previously and used in the subsequent experiments. In other respects the apparatus was the same. All the experiments were carried out at the temperature of 25° C. It is of course necessary to keep the temperature very constant during an experiment, as the apparatus acts like a gas-thermometer.

The following times of effusion were observed :—

	m.	s.	m.	s.
Hydrogen	3	47·9,	3	47·8
Oxygen	12	21·3		
Carbon monoxide .	11	16·4,	11	18
Nitrogen	11	18,	11	17·8.

It is evident from the results for hydrogen and oxygen that there is a large viscosity-effect. Thus for pure effusion the time for hydrogen should be very nearly one-quarter of that for oxygen, *i. e.* $3^{m}\ 5^{s}{\cdot}3$. It was found, however, that the effect of viscosity could be allowed for by employing, instead of the equation $t = \kappa\sqrt{d}$, where $d =$ relative density and $\kappa =$ a constant depending on the apparatus, the equation

$$t = \kappa_1\sqrt{d} + \kappa_2\mu,$$

where $\mu =$ relative viscosity, and κ_1, $\kappa_2 =$ apparatus-constants.

Thus if we employ the table of relative viscosities given by Graham [*], viz. :—

Oxygen . . . . . . = 1
Hydrogen . . . . . = ·4375
Nitrogen or CO . . = ·8750
CO_2 . . . . = ·7272

we can use the results obtained with oxygen and hydrogen to calculate κ_1 and κ_2. We obtain the equations

$$\kappa_1\sqrt{1{\cdot}008} + {\cdot}4375\,\kappa_2 = 227{\cdot}9,$$
$$4\kappa_1 + \kappa_2 = 741{\cdot}3,$$

from which

$$\kappa_1 = 129{\cdot}2, \quad \kappa_2 = 224{\cdot}4.$$

Hence the time of effusion for carbon monoxide should be given by

$$t = \sqrt{14}\,.\,129{\cdot}2 + {\cdot}875 \times 224{\cdot}2,$$

whence

$$t = 11^{m}\ 19^{s}{\cdot}6.$$

The difference between this and the observed time is about 3 per cent. In the case of nitrogen the agreement is a little closer, for here the calculated time is also $11^{m}\ 19^{s}{\cdot}6$, while the mean observed time is $11^{m}\ 17^{s}{\cdot}9$. A similar result is obtained by using von Obermaier's * values for the relative viscosities. For the purpose of comparing argon and helium with oxygen it was necessary to reduce the viscosity-correction as much as possible, so no further experiments were carried out with this form of effusion-plug. Microscopic examination showed that the hole produced by the spark was irregular in shape and more of the nature of a series of cracks or fissures than anything else. These are no doubt of excessively minute width and so, even with thin-walled glass bulbs, relatively high viscosity-effects are unavoidable.

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[*] "On the Motion of Gases," Part II., Phil. Trans. 1849, pp. 349–392.

The new effusion-plug was made by taking a circular disk of platinum-foil (about $\frac{1}{25}$ millim. thick), backing it with a flat piece of agate, and piercing it in the centre by gently pressing a very fine needle against it. The disks so constructed were then tested by sealing them to the end of a glass tube with Chatterton cement, and observing the rate of effusion into the exhausted vessel of a Töpler pump, by noting the rate of fall of the mercury in the vertical capillary.

A suitable disk having been obtained, it was melted off, burnt clean, and soldered with gold to the end of a stout platinum tube, which was finally sealed on to the end of the glass tube *w* (see figure). The effusion-aperture employed in the first series of measurements was about $\frac{1}{50}$ millim. in diameter. Preliminary experiments showed that the time of effusion for any given gas varied somewhat from day to day and—to a less degree—even during the course of a consecutive series of measurements. This source of error was eliminated by comparing each gas directly with oxygen, and usually the time of effusion for oxygen was measured immediately before and immediately after that of the gas in question, and the mean of these two values taken.

The first effusion measurements were made with oxygen and hydrogen to enable the viscosity-correction to be applied. The results were as follows :—

Oxygen $10^{m}\ 54^{s}{\cdot}7$ $10^{m}\ 54^{s}{\cdot}8$, $10^{m}\ 54{\cdot}8$.
Hydrogen $2^{m}\ 45^{s}$.

The time for hydrogen calculated from the densities alone is $2^{m}\ 44^{s}{\cdot}4$. The apparatus is therefore practically free from viscosity and no correction is required.

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* *Wiener Berichte*, Bd. lxxiii.; Carl's *Repertorium*, Bd. xiii.

The apparatus was left filled with hydrogen overnight, whereupon measurements of the effusion rate of hydrogen on the following day showed that some disturbance had occurred :—

m. s.
2 50·8
2 51·5
2 52·7

It appears very probable that the platinum had occluded some hydrogen, and that the resulting volume-changes were the source of the variations. The apparatus was now allowed to remain exhausted overnight. Experiments with oxygen next morning gave the following results :—

	m. s.
Half-an-hour after introduction of gas. .	10 57·8
1½ hours " " " . .	10 57·3
Apparatus left exhausted for an hour and fresh oxygen introduced	10 56·5

The apparatus was left filled with oxygen overnight, pumped out the next morning, allowed to remain in connexion with the pump for an hour or so, and then refilled with oxygen :—

Oxygen . . . $10^{m}\ 56^{s}{\cdot}2$, $10^{m}\ 56^{s}{\cdot}6$.

It was accordingly concluded that the aperture had been again brought to a constant state and any occluded hydrogen removed. Argon was now measured :—

Oxygen . . . . $10^{m}\ 56^{s}{\cdot}4$.
Argon . . . . . $11^{m}\ 47^{s}$, $11^{m}\ 47^{s}$.

According to the densities alone the time for argon should be

$$656{\cdot}4 \times \sqrt{\frac{19{\cdot}957}{16{\cdot}0}} = 12^{m}\ 13^{s}{\cdot}1.$$

That is to say, argon effuses *too rapidly* by about 3·5 per cent. when compared with oxygen by the inverse square-root law.

In order to confirm this result a second determination was made. During the interval (week-end) the apparatus had remained exhausted and, as will be seen, the time of effusion for oxygen had considerably increased :

	m.	s.
Oxygen	11	13·3
Argon	12	3·9
Oxygen	11	12
Mean oxygen	11	12·6

The time for argon, calculated from that for oxygen by means of the densities, is $12^{m}\ 31^{s}\cdot2$, so that the observed time is 3·7 per cent. less, which agrees fairly well with the previous result.

This deviation being in the direction indicated by the adiabatic theory, the next thing was to measure some other gas with a diatomic molecule and specific-heat ratio 1·4 ; for in that case agreement might be expected between the observed and calculated values. Experiments with CO gave the following results :—

	m.	s.	m.	s.
Oxygen	11	17·2		
CO	10	29·5	10	30·6
Oxygen	11	16		
Mean time for oxygen	=		11	16·6
Mean time for CO	=		10	30

The calculated value for CO is $10^{m}\ 32^{s}\cdot9$. The observed value is only ·4 per cent. smaller. Probably this deviation is due to experimental error (compare the two results with argon).

The next gas investigated was carbon dioxide ; for as this possesses a lower specific-heat ratio than 1·4, its time of effusion ought to be *greater* than that calculated. Experiment proved the contrary :—

	m.	s.	m.	s.
Oxygen	11	16·3		
CO_2	12	59	12	58·9
Oxygen	11	15·3		
Mean value for oxygen	11	15·8		

The value calculated for CO_2 is

$$675\cdot8 \times \frac{\sqrt{22}}{4} = 13^{m}\ 12^{s}.$$

The observed time is 1·7 per cent. *less.*

This was confirmed by a second measurement with a fresh preparation of CO_2 :—

	m.	s.
Oxygen	11	18·7
CO_2	13	2
Oxygen	11	18
Calculated for CO_2 from oxygen	13	15·4

Here, again, the observed time per cent. is 1·7 per cent. less.

This deviation * being in the opposite direction to that indicated by the adiabatic theory, it was considered advisable to re-examine the viscosity-relations of the apparatus. Results :—

	m.	s.
Oxygen	11	16
Hydrogen	2	51·6
Oxygen	11	16
Calculated for hydrogen by densities	2	49·7

These results indicate the presence of a small viscosity-effect. This was probably caused by the gradual narrowing of the aperture, which is shown by the successive results for oxygen. Now all the previous calculations have assumed the absence of any disturbance due to viscosity. The best way to determine their value is to re-calculate the experimental results, introducing a correction for viscosity as determined by these last measurements, *i. e.* introducing a *maximum* correction. This could be done directly by means of the formula

$$t = \kappa_1 \sqrt{d} + \kappa_2 \mu,$$

provided κ_1 and κ_2 remained constant. But the results for oxygen show that this was not the case. It is probable, however, that any change in the size of the hole will chiefly affect κ_1, since the outflow is mainly an "effusion" flow. These considerations suggest the following method of making the viscosity-correction. Calculate values for κ_1 and κ_2 from the last measurements for oxygen and hydrogen. Then in any particular case correct the value of κ_1 so obtained by assuming that the change in κ_1 is proportional to the change in the observed time of effusion for oxygen. That this mode of procedure is justifiable is shown by the fact that the times calculated for oxygen with the values of κ_1 and κ_2 so obtained agree very closely with the observed times in each particular case.

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* Graham found a similar deviation in the case of CO_2. He used brine, however, instead of mercury as enclosing fluid, and ascribed the deviation to the solution of the CO_2 in the brine (a single experiment lasted about an hour).

The last results for oxygen and hydrogen give $\kappa_1 = 166{\cdot}5$, $\kappa_2 = 10$. Accordingly the corrected time for CO (see p. 126) is given by

$$t = \left(166{\cdot}5 \times \frac{676{\cdot}6}{676{\cdot}0} \times \sqrt{14}\right) + ({\cdot}875 \times 10),$$

whence

$$t = 10^{\mathrm{m}}\ 32^{\mathrm{s}}{\cdot}3.$$

The following short table will serve to show the extent to which the correction affects the results :—

	m. s.	m. s.	m. s.	per cent.
Argon*	12 3·9	12 31·2	12 31	3·6
Carbon monoxide ...	10 30	10 32·9	10 32·3	0·36
Carbon dioxide.........	13 2	13 15·4	13 11	1·1

The first column gives the observed time, the second the time calculated from the densities alone, the third the calculated time corrected for viscosity, and the fourth the percentage deviation of the observed time from the time so corrected. In the case of argon and carbon monoxide the correction is quite negligible. For CO_2 it amounts only to ·5 per cent. The conclusions previously drawn remain therefore unaffected.

With regard to CO_2, the want of agreement between theory and experiment may possibly be due to the fact that this gas departs too much from the simple laws of the ideal gas.

In the case of argon the time of effusion, as calculated from that of oxygen according to the theory given by Hugoniot and Osborne Reynolds, is $11^{\mathrm{m}}\ 55^{\mathrm{s}}$†. It is only to be expected that the observed value would be greater, as the phenomenon is probably something intermediate between isothermal and adiabatic*.

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* The viscosity of argon referred to oxygen was obtained by combining Lord Rayleigh's value referred to air with Graham's value of air referred to oxygen. The result is $1{\cdot}21 \times {\cdot}901 = 1{\cdot}09$.

† According to Parenty's formula, it is $11^{\mathrm{m}}\ 31^{\mathrm{s}}{\cdot}7$.

A sample of helium was now introduced into the apparatus. After the effusion had proceeded for a short time, a complete block occurred. The helium was pumped out, and the mercury having been sucked out of the seal, the apparatus was cut above the tap and the effusion-plug removed for examination. There was a whitish deposit on the platinum. The hole was cleared by cautiously heating the platinum to redness and drawing air through it. On sealing the apparatus together again the hole was found to be clear, but on again admitting the helium another block occurred. It was evident that the helium contained some impurity which attacked the platinum or condensed in some way in the aperture. The helium was accordingly removed and the hole again cleared out as described. On sealing together again and testing with oxygen and hydrogen, a greatly increased viscosity-effect was observable. When the effusion-tube was cut out and the platinum foil microscopically examined, the cause of the viscosity could be seen in the form of *two* holes connected by a fissure. This was probably due to the corroding action of the impurity * combined with the frequent heating.

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* A few words of explanation are necessary here. In the first place, the mass-efflux on the assumption that the phenomenon is *isothermal* may be found as follows :—Employing the equation $\int\frac{dp}{\rho}+\frac{1}{2}q^2=\text{const.}$, which holds along a stream-line for steady irrotational motion, we obtain on integrating, since $p=\rho\text{RT}$, $q=\sqrt{2\text{RT}\log\frac{\rho}{\rho}}$, where ρ_0=density of quiescent gas in the reservoir. If the velocity, density, and sectional area at the vena contracta be denoted by q', ρ', and S' respectively, then mass-efflux $=q'\rho'\text{S}'$. From the condition $\frac{d}{d\rho}(q\rho)=0$, we find $\log\frac{\rho_0}{\rho'}=\frac{1}{2}$ and therefore $\text{S}'q'\rho'=\frac{\text{S}'\rho_0}{\sqrt{e\text{RT}}}$. Thus comparing two gases between the same pressure-limits during the period of constant efflux, $\frac{t_1}{t_2}=\sqrt{\frac{\rho_1}{\rho_2}}$, as already stated.

The equation given by Parenty being based neither on the assumption of an adiabatic nor an isothermal efflux, and being in fact practically an empirical equation, not much importance need be attached to the fact that it yields a value which is very sensibly smaller than that observed.

It must be noted that on the assumption of constant temperature, the velocity of the gas at the vena contracta is *less* than the velocity of sound in gas of that density and pressure, being in fact equal to the Newtonian value.

A new disk of foil was now pierced and soldered on to the platinum tube; but it was also found to show a very high viscosity-effect. The origin of this was finally traced to the cracking of the enamel at the junction of the platinum and glass tubes.

Owing to the difficulty of making this joint, a new effusion-plug was constructed as follows:—A thick circular disk of platinum was made by welding several pieces of foil together. A circular hole was punched in the centre of this, and a thin† disk of foil, which had been punctured in the manner previously described, was welded on so as to cover the hole in the thick disk. The latter was then fastened by means of Chatterton cement to a glass tube whose end had been turned over and ground to a flat flange; and this tube was sealed to the rest of the apparatus. After some trials an effusion-plug was obtained which showed only a comparatively small viscosity-effect:—

	m.	s.	m.	s.
Oxygen	4	3·1		
Hydrogen . . .	1	2·2	1	3·3
Oxygen	4	3		

A repetition of this test on the following day gave:—

	m.	s.
Oxygen	4	2·9
Hydrogen . . .	1	3·3

These results lead to a much higher viscosity-correction than in the case of the effusion-plug first used. We get $\kappa_1=57{\cdot}6$, $\kappa_2=12{\cdot}4$. Measurements with cyanogen gave the following results:—

	m.	s.	m.	s.
Oxygen	4	5		
Cyanogen	5	4·9	5	4·2
Oxygen	4	4		
Mean time for Cyanogen .	5	4·6		

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* A piece of glass which was immersed in the helium was found to fume in the air. As oxygen had been previously removed from the helium by burning phosphorus, the impurity was probably some volatile lower oxide of phosphorus.

† This was the thinnest foil procurable from Johnson and Matthey that was free from microscopic holes. It was about $\frac{1}{1000}$ in. thick.

Graham gives ·506 for the viscosity of cyanogen referred to oxygen. The calculated value is therefore

$$t=\left(\sqrt{26}\times 57{\cdot}6\times\frac{244{\cdot}5}{243{\cdot}0}\right)+(12{\cdot}4\times{\cdot}506) = 5^{\text{m}}\ 1^{\text{s}}{\cdot}8.$$

There is a deviation here of ·9 per cent. in the direction of *slower* effusion. The time calculated from the densities alone is $5^{\text{m}}\ 11^{\text{s}}{\cdot}6$.

The helium previously used was sparked over potash with oxygen and the oxygen removed by heated copper. After being dried by P_2O_5 it gave the following results :—

	m.	s.
Oxygen	4	3·8
Helium	1	37·1
Oxygen	4	3·4

The viscosity of helium referred to air was found by Lord Rayleigh to be ·96, so that its value referred to oxygen is ·865. The density of this specimen of helium was determined and found to be 2·314, so that it contained a considerable amount of argon. The calculated time is $1^{\text{m}}\ 38{\cdot}6$, from which it would appear that the helium effuses 1·5 per cent. faster than as calculated. This helium after being further dried over P_2O_5 was examined again, with the following result :—

	m.	s.
Oxygen	4	3·2
Helium	1	37·6
Oxygen	4	4·0
Helium (calc.)	1	38·4
Helium (calc. from density only) .	1	32·6

Here the deviation only amounts to ·8 per cent., which is about half the previous amount. Possibly this want of agreement in the results is partly due to the increased likelihood of error in noting the points of passage owing to the very rapid rate of effusion.

Owing to the high viscosity-correction it was thought advisable to re-measure argon and carbon monoxide as a check on the results given by this effusion-plug. Results :—

	m.	s.	
Oxygen	4	3·8	
Argon	4	21·1	(density 19·71)
Oxygen	4	3·4	
Argon (calc.)	4	29·9	3·3 per cent. faster.

Oxygen	4	3·2
CO	3	46·4
Oxygen	4	3·4
CO (calc.)	3	46·6

These results are in fairly close accordance with those previously obtained*, so that the method of correcting for viscosity appears to be justified in the main.

Owing, however, to the unpleasant prominence of the viscosity-correction in the case of helium, several attempts were made to obtain a better effusion-plug. An aperture was finally obtained showing a much smaller viscosity-effect. The pierced disk of thin foil was sealed transversely in a tube of flint-glass and the latter sealed on to the rest of the apparatus. This forms the simplest and most secure method of attaching the platinum-foil disk to the effusion apparatus. With hydrogen and oxygen the following results were obtained :—

	m.	s.
Hydrogen	2	7·9
Oxygen	8	21·3

The time for hydrogen calculated from the densities is 2$^{\mathrm{m}}$ 5$^{\mathrm{s}}$·8, so that a small viscosity-effect still exists. These results give $\kappa_1=122{\cdot}5$, $\kappa_2=11{\cdot}3$. Helium and argon were now remeasured.

Helium.—Density 2·314.

	m.	s.	m.	s.
Oxygen	8	22·2		
Helium	3	16·8,	3	16·6
Oxygen	8	24·2		

	m.	s.
Mean time for He observed	3	16·7
Time calculated with viscosity-correction	3	16·7
” ” from densities alone	3	11·2

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* As evidenced by the density, this specimen of argon was not very pure. It probably contained some hydrogen. This would account for the rather low “deviation” of 3·3 per cent.

Argon.—Density 19·71.

	m.	s.	m.	s.
Oxygen . . .	8	24·2		
Argon . . .	9	0·6,	8	59·5
Oxygen . . .	8	23·8		

	m.	s.
Mean time for argon (observed) . . .	9	0
Calculated from densities alone . . .	9	19·4
„ with viscosity-correction . .	9	19·2

These results show that in the case of argon the correction is negligible and that the observed time is 3·4 per cent. less than the calculated time, which is in good agreement with former results. In the case of helium the viscosity correction is still considerable and, contrary to previous results, the observed and calculated values agree.

After these measurements the times for oxygen and hydrogen were again determined :—

	m.	s.	m.	s.
Oxygen . .	8	23·9		
Hydrogen. .	2	6·6,	2	6·8
Oxygen . .	8	23·3		

The time for hydrogen calculated from the densities is $2^{\mathrm{m}}\,6^{\mathrm{s}}{\cdot}4$, so that there now appeared to be practically *no* viscosity-effect. Under these circumstances it appears difficult to say what sort of correction ought to be applied to the last-obtained results for helium. In order to try and clear up this difficulty a fresh series of measurements was made, with the following results :—

Argon.—Pure specimen, density 19·96.

	m.	s.
Argon	9	1·4
Mean oxygen	8	22·8
Argon (from densities)	9	21·6
Argon (corrected for viscosity) .	9	21·4

Observed rate 3·5 per cent. faster than calculated rate.

Helium.—Purer specimen, density 2·139.

	m.	s.
Oxygen	8	22·8
Helium	3	7·8
Oxygen	8	22·6

	m. s.
Helium (calculated from densities) . .	3 3·8
Helium (with viscosity correction) . .	3 9·4

Carbon monoxide.

	m. s.	m. s.
Oxygen . . .	8 23·6	
CO	7 49·8,	7 49·2
Oxygen . . .	8 22·7	

	m. s.
Mean time for CO	7 49·5
Time calculated from densities . .	7 50·7
Time calculated with viscosity . .	7 49·9

The results obtained for argon and carbon monoxide are in agreement with former ones. If we apply no viscosity-correction, then the helium effuses *slower* than as calculated. The want of agreement between this and former results may be partly due to variable admixture with argon.

The fact remains that all the results obtained for helium are affected by a more or less uncertain correction for viscosity, and do not agree among themselves. If any one were to be selected as better than the rest, it would be the last one, as the hole appeared to be practically free from viscosity-effects in this case, and the specimen of helium was pretty pure.

Saint-Venant and Wantzel's Phenomenon.

It was stated at the beginning that the dimensions of the apparatus were chosen so that the measurements lay in the region where the rate of effusion was independent of the back-pressure. This was frequently confirmed by experiment. The following results, obtained in the last series (where the back-pressure rose from 0 to 47·5 millim. during the course of a measurement), will serve to confirm the statement made above.

Oxygen.

Time of Effusion.	Back-pressure.
m. s.	
8 23·3	0 –47·5
8 23·5	47·5–93·9
8 25·3	93·9– —

In this series of experiments the final back-pressure was 47·5 millim. as already stated, and the initial and final pressures in the gas-reservoir 525 millim. and 322 millim. respectively. In the other series the final back-pressure was 60 millim., and the initial and final pressures in the gas-reservoir 690 millim. and 484 millim. These numbers are only approximate and intended merely to show the pressure-conditions under which the experiments were conducted.

The Joule-Thomson Effect.

As foreseen by the theory, the rate of effusion of argon, when compared with that of oxygen, is very considerably greater than the value as calculated by the law of the inverse square root of the density. The foregoing experiments agree uniformly in showing that the deviation amounts to 3½ per cent. On the other hand, the results obtained with helium, although not very uniform, show pretty conclusively that its behaviour is unlike that of argon. According to the theory, however, it should behave in an exactly similar manner. These facts seem to point to the omission of some factor or factors in the basis of the theory.

Now it will be observed that the theory assumes that the gases obey the ideal gas laws, and hence excludes anything of the nature of the Joule-Thomson effect. It therefore appeared of interest to examine the question of the effusion of an *imperfect* gas, with special reference to the Joule-Thomson effect.

An application of the equation of continuity and the law of conservation of energy to the issuing jet yields the well-known fundamental equation :—

$$\tfrac{1}{2}q^2 + U + pv = \text{const.},$$

where q = velocity,
U = internal energy per unit of mass,
v = specific volume,
p = pressure.

It is possible* to find an approximate expression for U by making use of the equation given by Joule and Thomson*, namely:—

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* *Cf.* Poincaré, *Thermodynamique.*

$$dT = \frac{K}{T^2}\,dp. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Choosing p and T as independent variables, we have

$$\frac{\partial}{\partial p}(U+pv)\,dp + \frac{\partial}{\partial t}(U+pv)\,dT = 0. \quad . \quad . \quad (2)$$

If we were dealing with an ideal gas, we should have

$$U+pv=CT, \quad \text{and} \quad \frac{\partial}{\partial t}(U+pv)=C,$$

where C = specific heat at constant pressure. This is not strictly applicable to the present case, but we may introduce it into (1) and obtain an approximation. From (1) and (2) we therefore obtain

$$\frac{\partial}{\partial p}(U+pv) = \frac{-KC}{T^2},$$

which on integration gives

$$U+pv = \frac{-KCp}{T^2} + f(T). \quad . \quad . \quad . \quad . \quad (3)$$

Employing (3) and the fundamental equation given above, we obtain an expression for the velocity of effusion which involves the constant of the Joule-Thomson equation:—

$$q^2 = 2[f(T_0) - f(T)] + 2KC\left(\frac{p}{T^2} - \frac{p_0}{T_0^{\,2}}\right). \quad . \quad . \quad (4)$$

For an ideal gas K = 0 and $f(T) = CT$. We may therefore write approximately:—

$$q^2 = 2C(T_0 - T) + 2KC\left(\frac{p}{T^2} - \frac{p_0}{T_0^{\,2}}\right).$$

The first term on the right-hand side was given by Saint-Venant and Wantzel. The second term appears, therefore, as a *correction-term* in a form involving the Joule-Thomson constant. The equation may also be written in the form

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* For the present purpose it was not thought necessary to use the formulæ recently proposed by Rose-Innes (Phil. Mag. March 1898), and by Love (Proc. Phys. Soc. vol. xvi. Dec. 1899, p. 454).

$$q^2=\frac{2\gamma}{\gamma-1}\left(\frac{p_0}{\rho_0}-\frac{p}{\rho}\right)+2\mathrm{KC}\left(\frac{p}{\mathrm{T}^2}-\frac{p_0}{\mathrm{T}_0^{\,2}}\right).$$

It is important to determine the *sign* of the correction-term. To do this it appears justifiable to assume the ideal gas laws, and so one has

$$2\mathrm{KC}\left(\frac{p}{\mathrm{T}^2}-\frac{p_0}{\mathrm{T}_0^{\,2}}\right)=2\mathrm{KCR}\left(\frac{\rho}{\mathrm{T}}-\frac{\rho_0}{\mathrm{T}_0}\right)$$

$$=2\mathrm{KCR}\frac{\rho_0}{\mathrm{T}_0}\left[\left(\frac{\rho}{\rho_0}\right)^{2-\gamma}-1\right].$$

Consider first the region where $2>\frac{p_0}{p}>1$. Since $\frac{\rho}{\rho_0}=\left(\frac{p_0}{p}\right)^{\frac{1}{\gamma}}$, it is clear that the expression in square brackets is *positive.* Consider next the region where the efflux is independent of the back-pressure.

From the equation

$$q^2=\frac{2\gamma}{\gamma-1}\left(\frac{p_0}{\rho_0}-\frac{p}{\rho}\right)+2\mathrm{KCR}\frac{\rho_0}{\mathrm{T}_0}\left(\frac{\rho^{2-\gamma}}{\rho_0^{\,2-\gamma}}-1\right)$$

we obtain

$$q^2\rho^2=\frac{2\gamma}{\gamma-1}\left(\rho^2\frac{p_0}{\rho_0}-k\rho^{\gamma+1}\right)+2\mathrm{KCR}\frac{\rho_0}{\mathrm{T}_0}\left(\frac{\rho^{4-\gamma}}{\rho_0^{\,2-\gamma}}-\rho^2\right),$$

where the laws of the ideal gas are assumed, and $\frac{p}{\rho^\gamma}=k$. To obtain the value of ρ at the vena contracta, it is necessary to differentiate with respect to ρ and equate to zero. This leads to the equation in ρ:—

$$\frac{\gamma}{\gamma-1}\left[2\frac{p_0}{\rho_0}-(\gamma+1)k\rho^{\gamma-1}\right]+\mathrm{KCR}\frac{\rho_0}{\mathrm{T}_0}\left[\frac{(4-\gamma)\rho^{2-\gamma}}{\rho_0^{\,2-\gamma}}-2\right]=0.$$

This equation is unfortunately not directly solvable; but its actual solution is unnecessary for the present purpose. The value of ρ given by it when substituted in the right-hand member of the preceding equation gives $q\rho$ at the vena contracta, and this multiplied by the sectional area S′ of the jet at that point gives the mass-efflux. From the above it is clear that in this case too the sign of the correction-term depends on K and the expression $\left[\left(\frac{\rho'}{\rho_0}\right)^{2-\gamma}-1\right]$. As before, we find that this expression is positive, since $\frac{p_0}{p'} > 1$, where p', ρ' denote the pressure and density at the vena contracta. The final result may be stated as follows:—"A gas will effuse *more rapidly* or *more slowly* than an ideal gas of equal density according as K is *positive* or *negative.*"

Now Joule and Thomson found K to be *positive* for all gases, with the exception perhaps of hydrogen. For hydrogen K was very small and its sign rather uncertain. Accordingly most gases will effuse in some degree *faster* than the usual theory of efflux would indicate. Now helium * is even more "perfect" than hydrogen. It is therefore just possible that for helium K is *negative*, in which case helium would effuse somewhat more *slowly* than the ordinary theory would indicate.

How far these effects would compensate each other, and in particular what the relative importance of the correction-term is, I have not yet investigated, but hope to do so in a subsequent communication.

Summary of Results.

1. Argon is found to effuse, when compared with oxygen, 3½ per cent. *faster* than as calculated by the law of the inverse square root of the density. This result is independent of any masking effect due to viscosity.

2. This result is in *qualitative* agreement with the adiabatic theory of the efflux of ideal gases, and is, if this may be granted, a confirmation of the high specific-heat ratio of argon.

3. When viscosity-effects are eliminated or allowed for, it is found that hydrogen, oxygen, and carbon monoxide effuse relatively in the manner predicted by the theory for ideal gases possessing the same, or nearly the same, specific-heat ratio.

4. Carbon dioxide, when compared with oxygen, appears to effuse about 1 per cent. *faster* than as calculated from the densities. This result is not in accordance with the adiabatic theory of the efflux of *ideal* gases.

5. The results obtained for helium are not uniform, and are affected by a viscosity-correction depending on an empirical

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* This has been shown by Professor Ramsay and Dr. Travers in a set of experiments (not yet published) on the compressibility of helium.

formula. They are sufficient, however, to show that the behaviour of helium is unlike that of argon, a result which is not foreseen by the theory.

6. If account be taken of the deviation of ordinary gases from the ideal laws, it is possible to obtain an expression for the efflux which contains a correction-term involving the constant K of the Joule-Thomson effect.

7. The sign of this correction-term shows that a real gas will effuse more *rapidly* or more *slowly* than an ideal gas of equal density and specific-heat ratio, according as K is *positive* or *negative*.

8. The suggestion is made that possibly the anomalous results obtained with carbon dioxide and helium may be thus explained. The deviations of the observed results from the results calculated for an ideal gas are, in the case of CO_2, in *qualitative* accordance with the theory proposed. In the case of helium they would be so if that gas possessed a negative K.

In conclusion I desire to express my deep sense of obligation to Professor Ramsay, at whose suggestion this investigation was begun, and whose valuable advice and assistance I enjoyed throughout its course.

I wish also to thank Dr. Travers for kind advice on many occasions. To Mr. E. C. C. Baly's great skill and constant advice and assistance I am more indebted than I can possibly say.

Chemical Laboratory,
University College, London.
December 1899.

Discussion.

Lord Rayleigh congratulated the author and pointed out that in the case of very small apertures the gas laws might not be obeyed. The ratio of the dimensions of the aperture to the length of the mean free path determined this, and not the ratio of aperture to molecular dimensions.

Prof. Ramsay and Prof. Everett expressed their interest in the work.

Dr. Donnan thanked Lord Rayleigh for his correction, and stated that the first aperture used was about $\frac{1}{50}$ mm. in diameter.

XI. *The Reversibility of Voltaic Cells.*

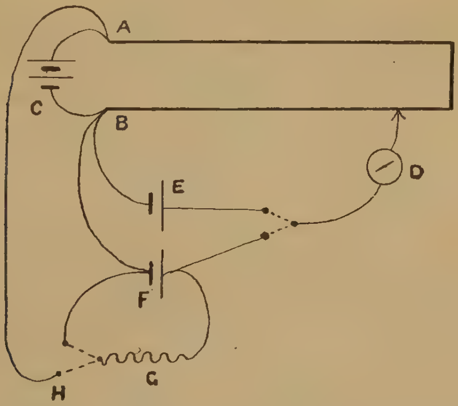
By T. SIDNEY MOORE*.

THE experiments described in this paper were carried out in order to test the reversibility of certain voltaic cells. Five cells have been treated:—Copper-zinc in sulphates, copper-cadmium in sulphates, copper-zinc in chlorides, and copper-cadmium in chlorides, in addition to the Clark cell. Preliminary experiments were carried out with nitrate cells, but the surfaces of the electrodes were spoiled by the nitrate solutions, and these cells have been put aside.

The diagram of the apparatus is shown in fig. 1.

ABCDEF shows the ordinary potentiometer arrangement, F being the experimental cell and E the Clark standard. G is an adjustable resistance, and by means of its three-way key H either the cell F may be placed in closed circuit with G, or the accumulators may be opposed to the experimental cell through the resistance G.

Fig. 1.



By means of this arrangement it is easy to get two determinations of the internal resistance of the cell F. Firstly, by means of the direct current when the cell F is in circuit with G, and, secondly, by means of the reading of the potentiometer when a current is running through F and in opposition to it.

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* Read March 2, 1900. (Communicated by Dr. Lehfeldt.)

But to calculate the internal resistance from the latter experiment it is necessary to assume that the experimental cell is reversible. Thus, if we assume that the cell is reversible, the difference between the values obtained for the internal resistance will measure the divergence of the cell from reversibility.

The results were calculated from formulæ which are easily deduced.

Let D = E.M.F. of experimental cell on open circuit.
D_1 = " " " when running through resistance R ohms.
D_2 = " " " when reversed through R ohms.
B = " " the accumulators.

Current from cell through $R = \frac{D}{R+r}$, where r is internal resistance of cell.

$$\therefore \quad \text{E.M.F. between poles of cell} = \frac{D}{R+r} \times R = D_1\,;$$

$$\therefore \quad r = \frac{D-D_1}{D_1} \times R. \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Or, if we regard the internal resistance as known, we have

$$D_1 = \frac{RD}{R+r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Now the reverse current through cell and resistance R ohms

$$= \frac{B-D}{R+r}, \text{ if the cell is reversible;}$$

$$\therefore \quad \text{External E.M.F.} = R \times \frac{B-D}{R+r}\,;$$

$$\therefore \quad \text{E.M.F. between poles} = B - \frac{R(B-D)}{R+r} = D_2\,;$$

$$\therefore \quad r = \frac{D_2-D}{B-D_2} R. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

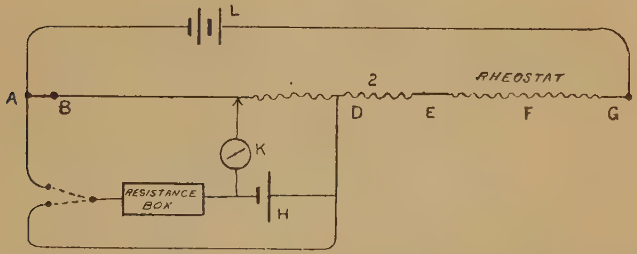
Or, if we regard the internal resistance as known,

$$D_2 = \frac{rB+RD}{r+R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

For the experiments a Crompton potentiometer was used, the arrangement of which is shown in fig. 2, together with the arrangement of the experimental cell and the resistance-box.

The accumulators L are connected with the circuit ABDEFG, and by means of the rheostat F and by balancing a Clark cell against the accumulators it is easy to so adjust the current that 1 millimetre of the bridge-wire shall correspond to a change in E.M.F. of 1 millivolt. The bridge-wire is 1 metre long, and thus corresponds to 1 volt. Also the coils (1) and (2) (see figure) are each of the same resistance as the bridge-wire, and thus each of these corresponds to 1 volt. So that it is very easy to get readings of any E.M.F. up to 3 volts.

Fig. 2.



The scale-wire extends to B, and the wire AB had a resistance equal to that of 43·4 millimetres of the scale-wire. Thus if the reverse current was taken between A and D, its E.M.F. was 2·0434 volts. If, however, as was sometimes the case, the coil (1) was taken out of the circuit, B was equal to 1·0434 volts.

The cell consisted of two glass vessels (short boiling-tubes) which had side-tubes blown in them. These side-tubes were connected by a short piece of indiarubber tube, to which was attached a screw-clip. It was found that, unless wads of cotton-wool were placed in the connecting-tubes, it was necessary to have solutions whose densities only differed in the fourth place. With the wads there is practically no diffusion, and the internal resistance is not unduly high. The solutions were made up approximately to the formula $R . 100 H_2O$, where R is the molecular formula of any salt. The densities were then adjusted until they were approximately equal.

Solution.	Density at 13°·5 C.	Solution.	Density.	Temp.
Copper sulphate ...	1·081	Copper chloride ...	1·074	25°
Cadmium " ...	1·082	Cadmium " ...	1·079	16
Zinc " ...	1·082	Zinc " ...	1·076	25

Results:—(1) Cu, $CuSO_4$, $ZnSO_4$, Zn. (Daniell's cell.)

R.	r (direct experiment).	r (reverse experiment).	D_1 (observed).	D_1 (calculated).	D (observed).	D_2 (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
4000 ...	1389	1392	0·8135	0·8135	1·3405	1·3397
6000 ...	1401·2	1389	0·8885	0·8895	1·2740	1·2736
12000 ...	1380·0	1378	0·9819	0·9835	1·1935	1·1937

For this cell D = 1·096 volt, B = 2·0434 volts.

The second column of the above was calculated from the observations by means of formula (*a*), the third column by (*c*), the fourth by (*b*), and the sixth by (*d*). The value of r used in the formulæ (*b*) and (*d*) was 1388·2, the mean of the six values obtained above.

In this experiment (and in all following) the copper electrode was electroplated and the zinc electrode cleaned with emery-paper and dilute sulphuric acid.

(2) Cu, $CuSO_4$, $CdSO_4$, Cd.

R.	r (direct experiment).	r (reverse experiment).	D_1 (observed).	D_1 (calculated).	D_2 (observed).	D_2 (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
4000 ...	1149·6	1150·6	0·5740	0·5746	·8070	·8068
6000 ...	1128·6	1151·1	0·6220	0·6206	·7880	·7878
12000 ...	1118·4	1168·0	0·6760	0·6746	·7660	·7654

For this cell D = 0·739 volt at 14° C., B = 1·0434.
Mean value for $r = 1144·4$.

The cadmium used was a rod prepared by Johnson and Matthey, and was warranted to be over 99 per cent. cadmium.

It was cleaned before each experiment by emery-cloth and dilute sulphuric acid.

(3) Cu, $CuCl_2$, $ZnCl_2$, Zn.

R.	r (direct experiment).	r (reverse experiment).	D_1 (observed).	D_1 (calculated).	D_2 (observed).	D_2 (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
4000 ...	304·9	301·4	0·997	0·9997	1·141	1·1302
6000 ...	286·8	298·5	1·025	1·0230	1·119	1·1182
12000 ...	262·0	304·3	1·051	1·0474	1·097	1·0961

For this cell D = 1·073 at 23° C., B = 2·0434.
Mean value of r = 293·1.

(4) Cu, $CuCl_2$, $CdCl_2$, Cd.

R.	r (direct experiment).	r (reverse experiment).	D_1 (observed).	D_1 (calculated).	D_2 (observed).	D_2 (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
4000 ...	479·9	482·0	0·671	0·6704	0·782	0·7836
6000 ...	487·8	487·3	0·695	0·6956	0·7725	0·7738
12000 ...	493·1	490·4	0·722	0·7227	0·762	0·7633

For this cell D = 0·752 at 16°·5 C., B = 1·0434.
Mean value of r = 486·75.

During the experiments, so long as diffusion was prevented, the E.M.F. of the cells remained constant. Even under the most unfavourable circumstances, viz. when the reverse current through 4000 ohms was running through the cell, the E.M.F. only altered about two millivolts. The conclusion to be drawn from the preceding results is that the cells treated, and consequently all similarly constituted cells, are reversible; for the differences in the values of the E.M.F.'s when calculated and when observed are not greater than might be expected as errors of experiment.

(5) A few experiments were also carried out with the Clark cell.

In the foregoing experiments the Clark standard consisted of two Clark cells in parallel. These were now separated, and one used as a standard and the other as the experimental cell. The internal resistance of this cell is, of course, comparatively small, so that it was necessary to use smaller resistances for R than were used in the previous cases. R was therefore made equal to 3000, 2000, and 1000 ohms respectively.

R.	r (direct experiment).	r (reverse experiment).	D_1 (observed).	D_1 (calculated).	D_2 (observed).	D_2 (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
3000 ...	92·9	98·8	1·389	1·3875	1·4515	1·4496
2000 ...	88·3	95·7	1·370	1·3667	1·4580	1·4585
1000 ...	......	95·1	......	......	1·4825	1·4837

For this cell D=1·4315 at 16° C., B=2·0434.
Mean value for r=94·16.

With R=1000 ohms, it was found that the current was much too large, as the E.M.F. of the cell decreased very rapidly when running the current. But the reverse current gave a fairly good result, as might be expected. For the direct current would cause the solution of Hg_2SO_4 to become weaker, and the solid present would not immediately saturate the solution. But the reverse current would cause Hg_2SO_4 to be formed in the solution, which would therefore deposit some solid, but would at the same time remain saturated. Thus, all the results from the reverse experiments are better than the corresponding direct results; but considering the nature of the cell, these latter are fairly good.

Thus we may say that the Clark cell, besides the others treated here and those similar to them, is reversible.

These experiments were carried out at the suggestion and under the direction of Dr. Lehfeldt, of the East London Technical College, to whom I gladly acknowledge my debt.

Physical Laboratory,
E. Lond. Tech. Coll., Oct. 1899.

Discussion.

Prof. S. P. Thompson asked if experiments had been made upon Leclanché cells, where the products of the action escape.

Dr. Lehfeldt said that experiments were not made upon these cells, because they were known not to be reversible.

XII. *The Coagulative Power of Electrolytes.* *By* W. C. D. Whetham, *M.A., Fellow of Trinity College, Cambridge.*

It has been found that electrolytes possess the property of coagulating solutions of colloidal bodies such as albumen and arsenious sulphide, and that their relative coagulative powers depend in a very striking manner on the valency of the metallic ion.

This coagulative action is of interest in certain physiological inquiries; and it was in connexion with some physiological work by Mr. W. B. Hardy [*] that the following suggestion originated. The matter, however, seems also to have some bearing on the theory of the physical nature of electrolytic solutions.

The coagulative power of a substance may be taken to be inversely proportional to the number of gram-equivalents which must be added to a definite solution of the colloid in order that immediate coagulation should follow. Thus, according to the experiments of Linder and Picton [†], the numbers expressing the concentrations of equi-coagulative solutions of various sulphates, when acting on arsenious sulphide, range round the following mean values for monovalent, divalent, and trivalent ions, the figure for aluminium chloride being taken as unity:—

$$930 : 26 : 0{\cdot}9.$$

The relative coagulative powers would be proportional to the reciprocals of these numbers, which are in the ratios

$$1 : 35 : 1023.$$

Again, Schulze [‡] found for solutions of chlorides coagulative powers in the ratios

$$1 : 30 : 1650.$$

These numbers are enough to show that the valency of the metallic ion has an effect on the coagulative power very different from that on properties for which the usual 1 : 2 : 3 ratios hold good.

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[*] Journal of Physiology, xxiv. p. 288 (1899).

[†] Journ. of the Chem. Soc. lxvii. p. 63 (1895).

[‡] *Journ. f. Prakt. Chem.* xxv. p. 431 (1882).

The coagulative powers of salts are certainly intimately connected with their electrical properties (see Hardy, *l. c.*); and an explanation of the curious valency relations must be sought by the light of our knowledge of the electrical nature of solutions.

Let us suppose that, in order to produce the aggregation of colloidal particles which constitutes coagulation, a certain minimum electrical charge has to be brought within reach of a colloidal group, and that such conjunctions must occur with a certain minimum frequency throughout the solution. Since the electrical charge on an ion is proportional to its valency, we shall get equal charges by the conjunction of $2n$ triads, $3n$ diads, or $6n$ monads, where n is any whole number.

In a solution where ions are moving freely, the probability that an ion is at any instant within reach of a fixed point is, putting certainty equal to unity, approximately represented by a fraction proportional to the ratio between the volume occupied by the spheres of influence of the ions and the whole volume of the solution, and may be written as Ac, where A is a constant and c represents the concentration of the solution. The chance that two such ions should be present together is the product of their separate chances, that is $(Ac)^2$. Similarly, the chance for the conjunction of three ions is $(Ac)^3$, and for the conjunction of n ions $(Ac)^n$.

In order that three solutions, containing trivalent, divalent, and monovalent ions respectively, should have equal coagulative powers, the frequency with which the necessary conjunctions should occur must be the same in each solution. We should then have, the constant being assumed equal in each case,

$$A^{2n}c_3^{2n} = A^{3n}c_2^{3n} = A^{6n}c_1^{6n} = \text{a constant} = B.$$

Therefore

$$c_3 = \frac{B^{\frac{1}{2n}}}{A}, \qquad c_2 = \frac{B^{\frac{1}{3n}}}{A}, \qquad c_1 = \frac{B^{\frac{1}{6n}}}{A},$$

c_1, c_2, c_3 representing the concentrations of monads, diads, and triads in their respective solutions.

Thus we get for the ratios of the concentrations of equi-coagulative solutions

$$c_1 : c_2 : c_3 = B^{\frac{1}{6n}} : B^{\frac{1}{3n}} : B^{\frac{1}{2n}} = 1 : B^{\frac{1}{6n}} : B^{\frac{1}{3n}}.$$

Put $B^{\frac{1}{6n}} = \frac{1}{x}$; the ratios can then be written

$$1 : \frac{1}{x} : \frac{1}{x^2}.$$

The reciprocals of the numbers expressing the relative concentrations of equi-coagulative solutions give values proportional to the coagulative powers of solutions of equal concentration; so that, calling the coagulative powers of equivalent solutions containing monovalent, divalent, and trivalent ions respectively p_1, p_2, p_3, we get

$$p_1 : p_2 : p_3 = 1 : x : x^2.$$

Let us now take some numerical examples. Putting $x=32$, we get the series

$$1 : 32 : 1024,$$

which agrees very well with Linder and Picton's results

$$1 : 35 : 1023;$$

and putting $x=40$, we get

$$1 : 40 : 1600,$$

numbers comparable to Schulze's values

$$1 : 30 : 1650.$$

No measurements appear to have been made on tetravalent ions, but it is easy to calculate their coagulative power on this hypothesis. Equal electrical charges would be obtained by the conjunction of three tetrads, four triads, six diads, or twelve monads. We should thus find:

$$c_1 : c_2 : c_3 : c_4 = B^{\frac{1}{12}} : B^{\frac{1}{6}} : B^{\frac{1}{4}} : B^{\frac{1}{3}}$$

$$= 1 : B^{\frac{1}{12}} : B^{\frac{1}{6}} : B^{\frac{1}{4}} : = 1 : \frac{1}{x} : \frac{1}{x^2} : \frac{1}{x^3},$$

if $B^{\frac{1}{12}}$ be put $=x$.

The coagulative powers are then in the ratios

$$p_1 : p_2 : p_3 : p_4 = 1 : x : x^2 : x^3.$$

Thus the first series of numbers becomes

$$1 : 32 : 1024 : 32800,$$

and the second $$1 : 40 : 1600 : 64000.$$

It is probable, therefore, that Linder and Picton would have found the coagulative power of the sulphates of tetravalent metals to be about thirty thousand times as great as that of the equivalent monovalent solution; while under the conditions of Schulze's experiments the result would probably have been about sixty thousand times that value.

My thanks are due to Mr. G. T. Walker for suggestions on the mathematical part of the reasoning given above.

October 6, 1899.

XIII. *On the Expansion of Porcelain with Rise of Temperature.* *By* T. G. Bedford, *B.A.*, *Sidney Sussex College, Cambridge.* (Communicated by Mr. E. H. Griffiths, F.R.S.)

In experiments involving the use of air-thermometers, such as comparisons between the air and platinum-resistance scales of temperature, a correction is required for the expansion of the thermometric envelope. Over a range at low temperatures the expansion might be readily determined, *e. g.*, by filling the bulb with a liquid, conveniently mercury, whose absolute expansion is known, and using it as a weight-thermometer to measure the relative expansion of the liquid. At high temperatures, however, such a method cannot well be used, and the correction must be calculated either from the results of low temperature measurements, or from the linear expansion as determined directly at these higher temperatures, provided the material be homogeneous. As porcelain is the substance generally used, this latter method is available; and it was therefore suggested to me by Mr. E. H. Griffiths, F.R.S., that it might be useful to try to determine how the expansion of porcelain varies with the temperature.

Direct determinations of the linear expansion of porcelain have been made by Deville and Troost (*Comptes Rendus*, lix. p. 162, 1864), and by Holborn and Wien (*Ann. Phys. Chem.* xlvii. p. 107, 1892). In the experiments of Deville and Troost on Bayeux porcelain the temperatures were measured by means of an air-thermometer heated in the same enclosure with the experimental rod, and having its bulb of the same kind of porcelain. Readings were taken at 0° C., and again at temperatures between 1000° and 1500°. The conclusion reached was that the coefficient of cubical expansion is constant, and between ·000016 and ·000017. In the experiments of Holborn and Wien the expansion of a length of 9 cm. of Berlin porcelain was measured, the temperature being determined by a thermo-electric junction in contact with the porcelain. Measurements were taken at the temperature of the room, and again at about 1000° in some experiments, at about 500° in others. As the values found for the mean coefficient for one of these intervals agreed as well with those found for the other interval as they did amongst themselves, these experimenters also concluded that the coefficient is constant. The mean value of the coefficient of linear expansion for the kind of porcelain used for their air-thermometers is taken as ·0000044.

The method adopted in the experiments described in the present paper was essentially the same as that employed in the case of *glass* by Callendar (Phil. Trans. 1887 A, p. 167), and by Callendar and Griffiths (Phil. Trans. 1891 A, p. 123).

A tube of glazed Bayeux porcelain about 1 metre long and 1·7 cm. external diameter was used. Two fine transverse scratches ran round the tube at a distance of about 91 cm. from each other; and the distance between these marks was directly compared at a series of temperatures from 0° C. to 830° C. with a standard length, by means of a pair of reading-microscopes.

The mean temperature of the portion of the tube between the marks was deduced from the resistance of a platinum wire (doubled for the sake of obtaining a convenient value for $R_{100}-R_0$) which passed straight down the tube from one mark to the other and back again. The wire was fastened down at intervals to a strip of mica which fitted the tube fairly tightly. At the upper mark the wires were attached to others of thicker platinum, which were themselves joined at the pyrometer-head which closed this end of the tube to copper leads. The head also carried a second pair of terminals to which was attached a thick platinum wire running to the upper mark and back to act as a "compensator."

Connexion was made between the pyrometer-head and the resistance-box by means of a carefully equalized and insulated fourfold cable. The lower end of the porcelain tube was closed by a porcelain plug.

The resistance measurements were made by the usual Wheatstone-bridge method, the arms of the bridge being equal. The resistance-box used contains a set of 7 coils of nominal values 10 to 640 mean box-units, and in series with the coils a bridge-wire 40 cm. long, the effective resistance of 1 cm. of which is equal approximately to 1 box-unit. By means of a vernier ·01 cm. can be read. The mean box-unit is roughly ·01 ohm *. A careful standardization of both coils and bridge-wire was made in January 1898, by Mr. E. H. Griffiths and Mr. C. F. Green; and again in May 1899, since the completion of these experiments, the coils have been restandardized by Mr. C. F. Green, and show no perceptible change since the previous standardization. The resistance of the pyrometer-wire was about 260 box-units at 0° C. The current from a dry cell through 20 ohms was employed, and was found to produce no serious heating-effect. Thermo-electric effects were eliminated by the use of Griffiths' Thermo-electric key (Phil. Trans. 1893 A, p. 398). A dead-beat mirror galvanometer was used.

The reading-microscopes, for the use of which the writer is indebted to Prof. Ewing, were made by the Cambridge Scientific Instrument Company. They were supported on solid stone blocks standing on a firm stone bench. The microscope-carriage moves along its slides by means of a screw of ·5 mm. pitch, the head being divided into 100 parts and

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* There is a full description of a box of this type, known as the "Student's Box," in the 'Electrical Review,' Aug. 18, 1899.

thus reading to ·005 mm. Tenths of these divisions could be estimated, but the diamond marks on the porcelain were not sufficiently good to enable settings of the cross-wire to be made to such accuracy. The gas-furnace in which the tube was heated was supported on a stand provided with levelling-screws, by adjusting which the marks were kept in focus as the tube was heated or cooled. Both the microscopes and bench were screened by bright tinned plate from the radiation from the furnace. As a standard length the distance between two diamond marks on a glass tube kept in a trough of melting ice was used. This distance was equal to 91·394 cm. During each experiment the readings for the glass tube were taken at intervals.

For the determination of the fixed points R_0 and R_{100}, the apparatus was more cumbersome than that used for smaller pyrometers. In determining R_{100}, steam from a boiler was led into a metal tube about 6 cm. in diameter surrounding the porcelain tube. The metal tube was surrounded by a similar wider tube 10 cm. in diameter and co-axial with it. The steam, passing along the inner metal tube, returned through the space between the two tubes, forming a jacket, and thence passed out to a condenser. A siphon-gauge showed any excess of steam-pressure within the apparatus above the atmospheric pressure. The jacketed steam vessel and the tubes leading from the boiler were carefully packed round with cotton-wool and hair felt. The steam-vessel was slightly inclined to the horizontal, so that the condensed water might drain away. It was found that with this arrangement the readings very soon became steady when steam was passed into the apparatus; and the values of R_{100} deduced from experiments on different days and under different barometric pressures agreed satisfactorily with one another.

The ice-point R_0 was determined by immersing the porcelain tube in a mixture of pounded ice and water contained in a vessel formed from the larger of the metal tubes used for the steam-point determinations.

The sample of platinum wire, from which the piece used in these experiments was cut, is known to have a value of δ, in Callendar's formula, from 1·50 to 1·51. The value $\delta = 1{\cdot}505$

was assumed, and thus a direct determination of the resistance at the temperature of boiling sulphur was avoided. An error of ·01 in δ causes an error of less than 1° in the calculated value of t at 1000°.

After a careful determination of the ice and steam points, the tube was heated as follows :—

TABLE I.

Number of Expt.	Date.	Maximum Temperature.	Number of Expt.	Date.	Maximum Temperature.
1...........	March 13.	77° C.	6...........	March 29	810° C.
2...........	„ 17.	319	7...........	„ 30.	824
3...........	„ 21.	650	8...........	April 3.	828
4...........	„ 23.	640	9...........	„ 7.	821
5...........	„ 24.	740	10...........	„ 8.	840

After the experiment of March 30, the ice and steam points were re-determined, and were found to have changed considerably. Accordingly, from this date, a re-determination of the fixed points was made after each exposure to a high temperature, and the values then obtained were used in the reduction of the observations of the preceding experiment. On account of the change, the observations of March 21–29 inclusive were not reduced.

In making an experiment the tube was heated to as high a temperature as possible, and observations of length and resistance were made. By diminishing the gas-supply the tube was then allowed to cool gradually, and when the temperature had become steady, length and resistance measurements were again made ; this process was repeated till the tube reached the temperature of the air. The observations were recorded thus :—

TABLE II.

Time.	Glass tube.	Bench.	Porcelain tube.	R. L.	Coils.	Bridge wire.	Temp. of Coils.
7.37 P.M.		14·65	10·1285	70, 50	D, H	+1·5	15·63
7.54 „	10·4212	14·65					
8.17 „		14·9	10·2045	60, 40	B, C, E, F, G	+3·6	14·9

Columns 2 and 4 give the sum of the microscope readings for the standard length and the porcelain tube respectively. The porcelain tube projected from the furnace so that a length of about 6 cm. at either end was not directly heated thereby. The temperature of the tube in the neighbourhood of the marks was taken roughly by means of mercury thermometers, and is recorded in column 5.

The results of experiments 1, 2, 7–10, are collected in Table III. (p. 155); the results of the last four experiments are represented in the diagram.

It appears from the diagram that, from 0° to 600°, the results are represented fairly well by a curve given by the formula

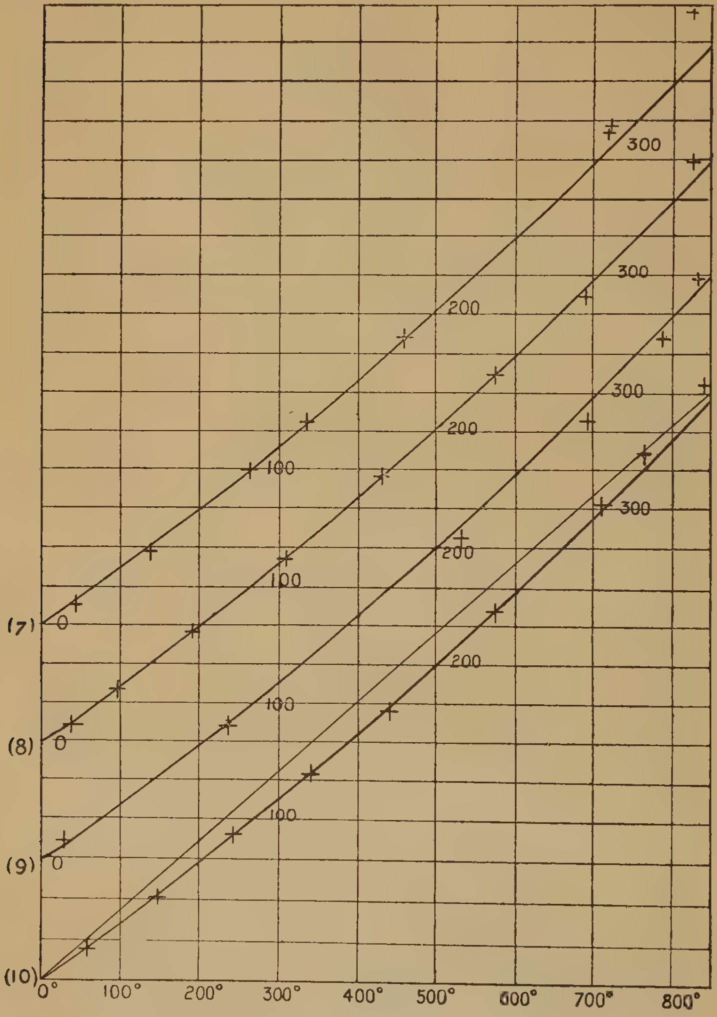
$$l_t = l_0(1 + 34{\cdot}25 \times 10^{-7}t + 10{\cdot}7 \times 10^{-10}t^2).$$

Above 600° the points are more erratic, but at these higher temperatures the length measurements were somewhat difficult to make; moreover, as no gas-regulator was available, it was impossible to keep the temperature quite steady during an observation. For comparison with the experimental numbers given in column 6, which represents the expansions reduced to unit length at 0° C., column 7 gives the corresponding values calculated from the formula; the full curves in the diagram are also drawn from the formula. The straight line in the diagram represents the expansion as given by Holborn and Wien's coefficient.

The coefficient of linear expansion at $t°$ C. is given by

$$\frac{1}{l_0}\frac{dl}{dt} = 34{\cdot}25 \times 10^{-7} + 21{\cdot}4 \times 10^{-10}t.$$

Since the coefficient varies with the temperature, an uncertainty is introduced due to the gradient of temperature from the portion of the tube heated in the furnace to the



Ordinates: expansion per unit length: unit 10^{-5}.
Abscissæ: temperatures centigrade.

(The straight line above the lower curve represents the expansion according to Holborn and Wien's coefficient.)

marks; but this uncertainty must be very small. According to a rough estimate made by the aid of the auxiliary temperature readings in column 5, Table II., the correction for the ends came out to be ·6 per cent. at mean temperature 800°, falling to ·4 per cent. at 600°.

TABLE III.

No.	Date.	R.	*t*.	Lengths in cm.	Expansion per unit length.	From formula.	
1.	Mar. 13	277·5	14·1	91·3728	6×10^{-5}	5×10^{-5}	l_0 91·3673 (1)
		341·0	77·4	·3910	26	27	R_0 263·073
2.	Mar. 17	274·7	11·4	·3716	4	4	R_{100} 363·358
		572·3	318·8	·4781	120	120	l_0 91·3683 (2)
7.	Mar. 30	1004·6	824·2	·7421	392·5	355	
		925·9	724·9	·6744	318·5	304·5	
		924·2	723·4	·6716	315·5	303·5	l_0 91·3833
		703·6	462·4	·5519	184·5	181	
		589·3	336·5	·5006	128·5	127·5	R_0 260·467
		520·7	263·0	·4733	98·5	97·5	R_{100} 361·788
		398·0	136·4	·4272	48	48·5	
		303·5	42·0	·3957	13·5	14·5	
8.	(Apr. 3	277·0	16·1	·3860	3	5·5)	
	Apr. 3	1005·4	827·5	·7165	372	357	
		898·2	692·5	·6381	286	288·5	
		801·4	576·3	·5912	235	233	l_0 91·3765
		675·1	431·5	·5318	170	167·5	
		561·7	307·3	·4834	117	115	R_0 260·875
		454·3	194·2	·4413	71	70·5	R_{100} 361·903
		360·7	98·8	·4084	35	35	
		299·0	37·3	·3877	12	13	
9.	Apr. 7	996·4	821·5	·7036	358	354	
		971·3	789·2	·6811	333·5	336·5	l_0 91·3765
		897·1	695·6	·6336	281·5	290	
		762·8	534·3	·5646	206	213·5	R_0 261·8
		495·3	237·7	·4552	86	87·5	R_{100} 362·115
		291·2	29·0	·3874	12	10	
10.	Apr. 8	1011·4	839·5	·7316	379·5	363	
		957·4	770·0	·6913	335·5	327	
		920·2	723·1	·6633	304·5	303·5	l_0 91·3848
		801·9	579·3	·6002	235·5	234·5	
		681·8	440·9	·5404	170·5	172	R_0 261·847
		593·4	342·5	·5030	129·5	130	R_{100} 362·306
		502·6	245·0	·4678	91	90·5	
		406·6	145·1	·4321	52	52	
		315·6	53·1	·4023	19	18·5	

The error introduced into the temperature measurements, if the part of the tube occupied by the wire did not precisely coincide with the part between the diamond marks, must also have been very small. Thus, for a temperature gradient so steep as 100° per centim. in the neighbourhood of the diamond marks, an error of 1° in the temperature would necessitate a displacement of the wire by nearly 1 centim. The chief difficulty in experiments of this kind seems to be in insuring that the temperature shall be uniform all along the tube. With an ordinary gas-furnace it is impossible to be certain that this condition is satisfied. An accident to the tube after experiment 10 prevented any further measurements, and so no experiments were made while the temperature was *rising*.

As may be seen from Table III., there seem to have been permanent changes in the length of the tube during the course of the experiments, but these changes are very small and apparently irregular. At the end of experiment 7 it was observed that the tube had become very slightly bent; the irregularities in the length at 0° may be due to this. The total increase in length at 0° from March 13 to April 8 was ·02 per cent.

For cubical expansions we get

$$v_t = v_0(1 + 102{\cdot}75 \times 10^{-7} t + 32{\cdot}4 \times 10^{-10} t^2);$$

and for the coefficient at t_0,

$$\frac{1}{v_0}\frac{dv}{dt} = 102{\cdot}75 \times 10^{-7} + 64{\cdot}8 \times 10^{-10} t.$$

In conclusion the writer must express his indebtedness for the use of the Sidney College Chemical Laboratory, and also for help which he has received from Mr. C. F. Green, B.A., from time to time.

XIV. *On the Distillation of Liquid Air, and the Composition of the Gaseous and Liquid Phases.*—PART I. *At Constant Pressure.* *By* E. C. C. BALY[*]. (Communicated by Prof. RAMSAY, F.R.S.)

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THE experiments described in this paper were commenced with a view of obtaining the relation between the temperature and the composition of the gas evolved from liquid air boiling under atmospheric pressure, so as to render possible the determination of the temperature of boiling air by the analysis of the gas evolved. They were, however, extended beyond this, and analyses were made of both the liquid and gaseous phases for all mixtures of oxygen and nitrogen, thus completing the investigation of the distillation of liquid air under constant (atmospheric) pressure.

The measurements of temperature were all made by means of a Callendar compensated hydrogen-thermometer. This instrument, which is a constant-pressure apparatus, differed from Callendar's description [†] in that the measurement of volume-change was read by admission of mercury into a graduated burette, instead of being weighed. The temperature as shown by Callendar may be calculated from the equation $T=\frac{V_0T_2}{V_1-V_2}$;

where V_0 is the volume of the thermometer-bulb ;

V_1 the total volume of the thermometer-bulb and the graduated burette ;

V_2 the volume of gas measured in the burette during the experiment ; and

T_2 the absolute (hydrogen) temperature of V_2.

In the thermometer used throughout the experiments, the volume V_0 (at 15°) was 28·655 c. c. and the total volume V_1 was 129·590 c. c. The adjustment in order to make both sides of the apparatus, *i. e.* the compensating side and the thermometer side, quite equal in volume, was very carefully performed by means of the burette and then connexion was opened between the two sections so as to ensure there being an equal mass of gas on each side. The filling with hydrogen was very carefully carried out. The whole apparatus was thoroughly exhausted, and pure hydrogen was admitted to approximately 760 mm. pressure. The hydrogen was prepared from the palladium alloy, the first fractions which came off the palladium being rejected, and was dried over phosphorus pentoxide. Every care was taken in the filling, and the thermometer was several times refilled during the work.

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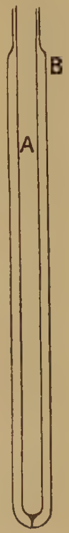
[*] Read March 2, 1900.

[†] Proc. Roy. Soc. vol. l. p. 247.

The correction for the contraction of the glass bulb was also determined, and an attempt was made to measure the coefficient of expansion of glass between the limits −190° C. and 20° C., the usual limits of the experiments. The apparatus was a very simple one, as shown in fig. 1, and depended on the contraction of a glass tube of known length. A tube A was taken, which just slipped through the contracted neck of the tube B. Both tubes were sealed at their lower ends, and A rested on the bottom of B by a fine glass point, to minimise heat-conduction as far as possible. The whole apparatus was dipped into liquid air, while water was kept running through the inner tube A, thereby cooling B while A was kept warm. The contraction suffered by B was measured by observing with a micrometer the distance between two lines, etched one on A and the other on B, before and during the cooling. The apparatus worked very well, and a satisfactory measurement was obtained in which the total length of B cooled was 89·0 cm. The mean linear coefficient found was ·0000073, Regnault's measurement between 0° and 10° being ·0000085.

Fig. 1.



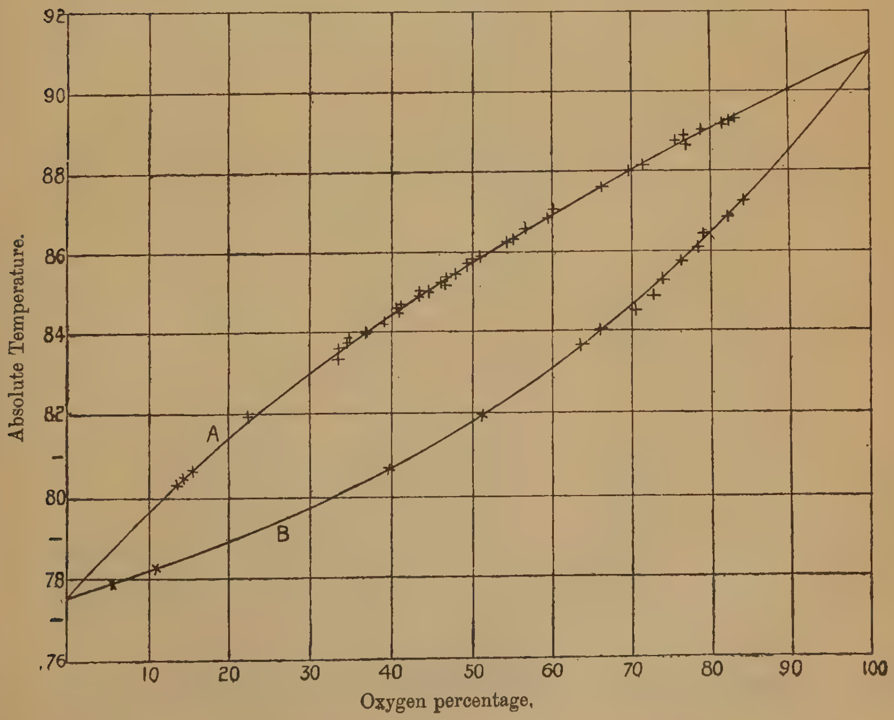
The measurements of temperature were corrected in accordance with the above found coefficient, the volume of the thermometer-bulb being taken as 28·655 (1 − ·0000219 t).

For the temperatures dealt with in these experiments the correction was about 0°·37.

The probable accuracy of the results with the thermometer may be judged from the volume of the thermometer-bulb, 28·655 c. c., which caused the probable error to be very small. The reading of the volume of the gas in the burette was certainly accurate to ·02 c. c., which means a maximum error of about 0°·02. In practice, however, the results agree better than this; for two determinations of the boiling-point of oxygen, and two of the boiling-point of nitrogen, differ respectively by only 0°·01, the measurements being made several days apart. The volumes of the various portions of the thermometer were most accurately determined, and there seems every reason to trust the measurements made with it. As regards the practical use of the instrument, too much cannot be said in praise of it. It is extremely quick to take up temperature-changes and very rapidly worked, and generally a most convenient and simple apparatus to use.

In the experiments on the composition of the vapour, the method of working was very simple. The thermometer-bulb

Fig. 2.



was immersed in the liquid air contained in a vacuum-jacketed vessel, the top of which was loosely stoppered with cotton-wool. Samples of the gas evolved were taken from time to time as the air boiled away, by means of a tube passing through the cotton-wool, and the thermometer reading was noted at each time. The samples of gas were afterwards analysed by means of burning phosphorus, and the results plotted as percentages of oxygen, against the corresponding absolute temperatures. Several series were thus obtained, and the ends of the curve, that is to say where the mixture contained great excess of nitrogen or oxygen, were obtained by mixing liquid oxygen or nitrogen, as the case might be, with the liquid air. The curve drawn through the points so obtained was completed by the determination of the boiling-points of nitrogen and oxygen, and it was found that the extrapolated curve met these points absolutely. The smoothed curve is shown on fig. 2 (curve A), with most of the observed points marked with a cross, many of which are double. This curve has been plotted on a much larger scale, and as it is likely to prove of use in any work connected with liquid air, the following points read therefrom will serve for its reproduction :—

Temperature (absolute).	Percentage of Oxygen.	Temperature (absolute).	Percentage of Oxygen.
77·54°	0·00 B.P. of Nitrogen.		
78·0	2·18	85·0°	44·25
78·5	4·38	85·5	48·17
79·0	6·80	86·0	52·19
79·5	9·33	86·5	56·30
80·0	12·00	87·0	60·53
80·5	14·78	87·5	64·85
81·0	17·66	88·0	69·58
81·5	21·22	88·5	74·37
82·0	23·60	89·0	79·45
82·5	26·73	89·5	84·55
83·0	29·95	90·0	89·80
83·5	33·35	90·5	95·10
84·0	36·86	90·96	100·00 B.P. of Oxygen.
84·5	40·45		

If the above points be plotted and the curve drawn, the complete relation will be obtained, and the temperature of boiling air can be read direct therefrom if the composition of the gas evolved be found.

In order to further investigate the subject, a similar series of experiments was carried out in connexion with the composition of the liquid phase and its relation to the temperature. The samples were taken by means of a finely drawn piece of capillary tubing which dipped into the liquid. This was connected with a filter-pump which was kept running during the experiments. Samples of the gas were taken from a T-piece between the capillary and the filter-pump. The liquid air did not fractionate in the capillary, but boiled rapidly away as it rose in the tube out of the vacuum-jacket; and samples were thus obtained of the mixture of oxygen and nitrogen which composed the liquid. Readings were taken as before on the thermometer, and the experiments were carried out, generally speaking, as in the case of the vapour phase above described. The results obtained were plotted, percentages of oxygen against temperature, and the curve thus obtained is shown on fig. 2 (curve B).

This curve has also been drawn on the large scale, and the following points read therefrom may be of interest:—

Temperature (absolute).	Percentage of Oxygen.	Temperature (absolute).	Percentage of Oxygen.
77°·54	0·00	84°·5	69·31
78·0	8·10	85·0	72·27
78·5	15·25	85·5	75·10
79·0	21·60	86·0	77·80
79·5	27·67	86·5	80·44
80·0	33·35	87·0	82·95
80·5	38·53	87·5	85·31
81·0	43·38	88·0	87·60
81·5	47·92	88·5	89·82
82·0	52·17	89·0	91·98
82·5	55·94	89·5	94·09
83·0	59·55	90·0	96·15
83·5	62·93	90·5	98·16
84·0	66·20	90·96	100·00

The two curves A and B represent the complete fractional distillation of any mixture of oxygen and nitrogen under 760 mm. pressure. For they show the boiling-point of every mixture of oxygen and nitrogen at 760 mm., and also the temperature at which any mixture of oxygen and nitrogen will liquefy and the composition of the liquid formed. It is evident that the lines of equal temperature cut the two curves at points of corresponding equilibria; that is to say, the compositions of liquid and vapour phases in equilibrium at each temperature. In connexion with these corresponding compositions of liquid and vapour, F. D. Brown * suggested that in a distillation of a mixture of two liquids under constant pressure, the following formula might express the relation between them :—

$$r' = r \times \frac{P_1}{P_2},$$

where r' is the ratio of components in the vapour phase, and r the corresponding ratio in the liquid phase, and $\frac{P_1}{P_2}$ the ratio of the vapour-pressures of the two components. This formula, however, assumes the validity of Raoult's law for every possible mixture. In an actual experiment, however, Brown found that it did not hold good, but that in the equation $r' = r \times C$, C was remarkably constant.

But this relation does not hold in the case of air, as the following results show :—

Temperature.	$\frac{r'}{r}$.	Temperature.	$\frac{r'}{r}$.
77°·9	·2416	86·4	·3141
78·2	·2495	88·2	·3274
78·5	·2582	89·2	·3406
79·9	·2710	90·1	·3592
81·4	·2828	90·5	·3725
83·2	·2934	90·7	·3806

It will be seen that $\frac{r'}{r}$, instead of being constant, has a steadily increasing value with rise of temperature.

Lehfeldt, in his paper on "The Properties of a Mixture of Liquids" †, showed that in Brown's case the logarithms of the ratios corresponding in the liquid and vapour phases

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* Chemical Society's Transactions, xxxix. p. 304.

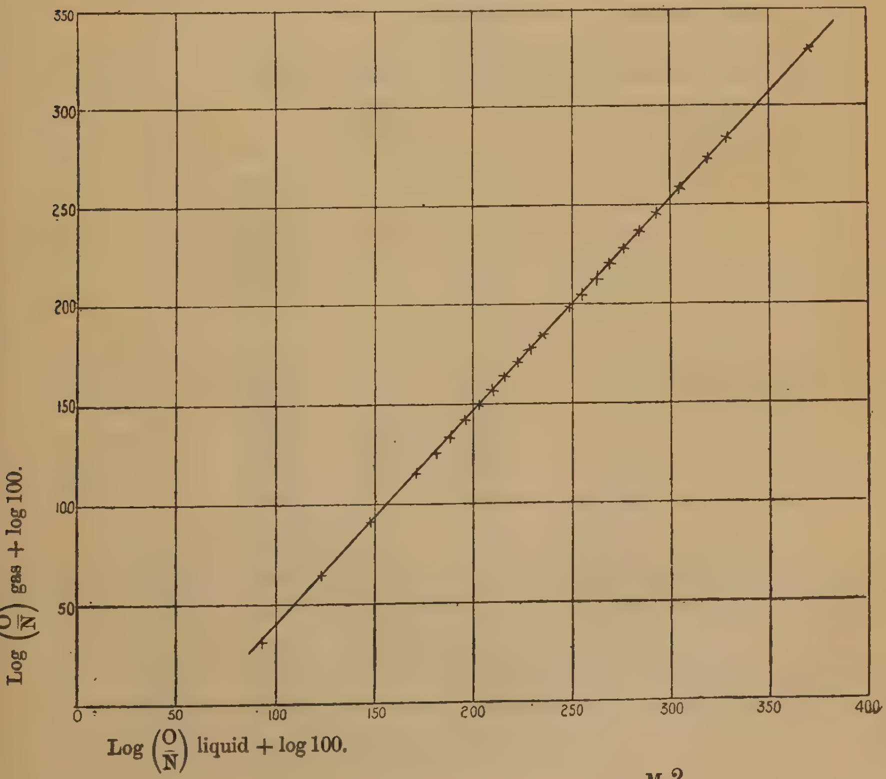
† Phil. Mag. [5] xl. p. 397.

had a linear relation; that is to say

$$\log r' = a + b \log r.$$

Inasmuch as this relation held so well for Brown's results, the logarithms of the corresponding ratios with air were plotted, and, as shown in fig. 3, a linear relation was found to exist in this case. The logarithms of 100 r and 100 r' were plotted for greater convenience. The points shown through which the curve is drawn were found for each half degree rise of temperature. The general accuracy of the results is shown by this curve, the departure of the points from the straight line being hardly appreciable. The large curves of percentages of oxygen against temperature

Fig. 3.—Relation between Logarithms of Ratios of Oxygen and Nitrogen in Gas and Liquid phases.



were smoothed to a slight extent by reference to the logarithmic curve, though this made no change except to remove two slight irregularities which had not before been noticed.

The values of the constants a and b in the equation $\log r' = a + b \log r$ were first calculated from two pairs of readings from the smoothed logarithmic linear curve. As, however, these did not agree very well, 22 readings were made, and the most probable value calculated by the method of least squares, which gave the results

$$a = \cdot 2097.$$
$$b = 1\cdot 06737.$$

The most probable relation, therefore, between the corresponding ratios throughout the distillation is

$$r' = \cdot 2097 \times r^{1\cdot 06737},$$

where $r' = 100 \times$ ratio in vapour,
and $r = 100 \times$ ratio in liquid.

The following series of calculated and observed ratios shows the accuracy of the above equation.

Temperature.	Ratio in Vapour. Observed.	Ratio in Vapour. Calculated.
79°	·073	·072
80	·136	·137
81	·215	·215
82	·309	·310
83	·428	·432
84	·584	·586
85	·794	·795
86	1·09	1·09
87	1·53	1·55
88	2·29	2·30
89	3·87	3·87
90	8·81	8·87

As regards the boiling-points of oxygen and nitrogen, the values given by previous experimenters differ to some extent from those given above, but they have not all been compared at the same pressure. Of the boiling-points of oxygen, the two latest are by Olszewski *, in his comparison of hydrogen

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* 'Nature,' liv. p. 377.

and helium thermometers, and by Estreicher* on the saturation pressures of oxygen. Olszewski's measurements were five in number, and the means from the two thermometers were as follows :—

Pressure.	Temperature abs.
741 mm.	90°·35
240 ,,	81·15
90·4 ,,	74·25
12·0 ,,	63·75
9·0 ,,	62·32

In order to complete the vapour-pressure curve for the above, the ratios of the temperatures giving equal vapour-pressures with water and oxygen were plotted against the water temperatures according to Ramsay and Young's equation†. The vapour-pressures of water were taken from Regnault's values as corrected by Broch. From the straight line passing through the points, data were calculated for the vapour-pressure curve. This was drawn, and gave the boiling-point at 760 mm. as 90°·60 absolute.

As regards Estreicher's measurements, of which there are 44, they have been plotted directly, but it is difficult to draw a curve through them for they are very scattered at the higher temperatures. The point he gives as the mean of 25 observations, P=743·8 mm. T=90°·44, agrees very well with Olszewski's values, and so do two more points. If, then, these points be taken as correct and the curve drawn, this can only be done by neglecting entirely many points at medium pressures. The curve, then, is almost superposed on Olszewski's. On the other hand, if the points at intermediate pressures be given some value, a very fair curve can be drawn which very nearly gives the same boiling-point as found on the Callendar thermometer as above, viz. 90°·96 abs., the actual point being 90°·90. Which curve to adopt as best expressing his results I do not know, for no data are given of the 25 observations whose mean is given as one point. The difference between the boiling-point I have given and that found by Olszewski is 0°·36.

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[*] Phil. Mag. [5] xl. p. 454.

[†] Ibid. [5] xx. p. 515, xxi. pp. 33, 135.

Of the boiling-point of nitrogen, Olszewski* gives a measurement in his series of five vapour-pressures, which are as follows :—

Pressure.	Temperature (abs.).
35 atmospheres	127°·0
31 „	124·8
17 „	116·5
1 „	78·6
60 mm. (melting-point)	59·0

The straight line of Ramsay and Young's ratios was drawn for these points. The last two by no means agree, and were therefore given equal weight. The vapour-pressure curve wrs drawn, and the boiling-point of nitrogen was given as 77°·38. The difference, therefore, between the boiling-point I have given and that obtained by smoothing Olszewski's numbers is 0°·16. Olszewski's values for the boiling-point, for the two gases are thus both lower than the ones I have found.

In order to test Brown's suggestion that the ratio of the partial vapour-pressures of the two components in the liquid directly determines the composition of the vapour, it was necessary to make measurements of the vapour-pressures of oxygen and nitrogen with the temperatures referred to the Callendar thermometer. Since these vapour-pressures were only required between the temperatures 77° and 91° absolute, two points on each curve were sufficient, and the complete curve was drawn by the Ramsay and Young method. Of these two points, the pressure of 760 mm. at the boiling-point was one, and for the other it was necessary to determine the vapour-pressure of each gas at the boiling-point of the other. This was carried out first for nitrogen by immersing a small bulb containing atmospheric nitrogen into pure liquid oxygen, and then measuring the pressure under which it liquefied.

The mean of four readings was p=2805·4 mm., T=90°·96.

This result very nearly lies on the curve of Olszewski's smoothed results.

The two points p=760 mm. T=77°·54 and p=2805 mm. T=90°·96 were plotted by Ramsay and Young's method, and the vapour-pressure curve drawn.

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* *Compt. Rend.* xcix. p. 133.

Vapour-Pressures of Nitrogen.

Temperature (absolute).	Pressure in mm.		
	Atmospheric.	Chemical.	Olszewski (Atmospheric).
77°	716·0	717·0	726·0
77·5	757·5	760·0	768·5
78	800·0	806·0	815·0
78·5	846·5	856·0	860·5
79	895·0	906·0	908·5
79·5	944·0	959·0	959·0
80	995·0	1013·0	1010·5
80·5	1048·0	1072·5	1065·5
81	1104·0	1130·5	1121·5
81·5	1163·0	1193·0	1180·0
82	1225·4	1258·0	1240·5
82·5	1290·0	1324·0	1304·0
83	1357·0	1386·0	1369·5
83·5	1426·0	1468·0	1438·0
84	1497·0	1544·5	1508·5
84·5	1570·5	1623·5	1582·0
85	1646·0	1705·5	1658·0
85·5	1725·0	1792·0	1737·0
86	1808·0	1880·0	1820·0
86·5	1895·0	1968·0	1904·5
87	1985·0	2062·0	1992·5
87·5	2076·0	2146·0	2081·0
88	2170·0	2256·0	2173·5
88·5	2267·0	2340·0	2268·0
89	2368·0	2465·0	2368·0
89·5	2472·5	2575·5	2472·0
90	2581·0	2686·0	2579·0
90·5	2694·0	2799·0	2688·0
91	2812·0	2916·5	2802·0
92·4	...	...	3125·0
94·1	...	...	3581·0
95·9	...	...	4088
97·6	...	...	4652
99·4	...	...	5274
101·2	...	...	5962
103·0	...	...	6717
104·9	...	...	7546
106·7	...	...	8644
108·6	...	...	9443
110·4	...	...	10520
112·3	...	...	11689
114·3	...	...	12956
116·2	...	...	14325
118·1	...	...	15801
120·1	...	...	17390
122	...	...	19097
124	...	...	20926

The vapour-pressures of chemical nitrogen were also determined. These were carried out similarly to those of atmospheric nitrogen with some intermediate points taken in liquid air. The boiling-point was not actually measured owing to the difficulty of preparing a sufficient quantity of liquid chemical nitrogen. The Ramsay and Young ratios were calculated and extrapolated to 760 mm., and from the straight line the vapour-pressures were obtained. The values obtained from the complete curve are given in the second column. Olszewski's values are continued up to 124° absolute.

The measurement of the vapour-pressure of oxygen was carried out very similarly to that of nitrogen. A large quantity of liquid nitrogen was made, and a small bulb connected with a store of pure oxygen from $KMnO_4$ was surrounded with it. When the bulb was about a quarter full of liquid oxygen, it was connected with a gauge and the pressure read. Two series of measurements were made with one preparation of oxygen, and a third with fresh oxygen prepared with the greatest care. All three agreed absolutely to a tenth of a millimetre. Great pains were taken with these measurements on account of their disagreement with both Olszewski's and Estreicher's. The result obtained was $p = 171{\cdot}7$ mm. $T = 78^\circ{\cdot}08$. Olszewski's and Estreicher's measurements were about 157 mm. at the same temperature. A very extraordinary faculty for being superheated was shown by the liquid nitrogen in these experiments. Although it was to all intents boiling, that is to say it was in actual ebullition, the temperature was $0^\circ{\cdot}8$ above the true boiling-point. By dropping in pieces of copper wire or glass the temperature at once fell to the normal boiling-point, but if left the nitrogen rapidly superheated itself, and the temperature rose to exactly the same point as at first. It appears, therefore, that unless these liquefied gases are in a state of extremely rapid ebullition, they become superheated to a very considerable extent. This may possibly be the explanation of Estreicher's and Olszewski's results for vapour-pressures of oxygen being so much lower than the one I have obtained. It is true that Estreicher and Olszewski agree very well in their values at low pressures, but this may be quite easily accounted for, because they used the same thermometer, and because in my results the superheating is always exactly the same in the same apparatus, and a small quantity of gas bubbled through the liquid, such as Estreicher

Vapour-pressures of Oxygen.

Temperature (absolute).	Vapour-Pressure.		
	1. (B.)	2. (Ols.)	3. (E.)
62°	...	8·4	9·6
63	...	10·8	11·0
64	...	13·3	14·6
65	...	16·1	17·7
66	...	19·7	21·2
67	...	24·0	25·6
68	...	29·1	31·0
69	...	35·6	37·2
70	...	43·0	44·6
71	...	51·6	53·0
72	...	61·0	62·5
73	...	72·0	73·5
74	...	85·0	86·0
75	...	100·0	100·0
76	...	117·5	116·0
77·0	138·4	136·2	134·0
77·5	158·7	146·5	145·1
78·0	170·0	158·0	155·7
78·5	181·4	169·8	167·5
79·0	193·5	182·5	180·0
79·5	206·6	195·9	193·9
80·0	220·0	210·1	208·1
80·5	234·0	224·8	222·8
81·0	249·0	240·1	237·9
81·5	264·8	257·0	253·7
82·0	281·8	274·0	270·0
82·5	299·5	292·1	287·5
83·0	319·2	311·7	305·3
83·5	338·6	332·0	323·3
84·0	359·0	353·5	342·3
84·5	380·5	376·4	362·0
85·0	401·8	401·7	382·9
85·5	424·6	427·0	404·6
86·0	449·0	454·0	427·4
86·5	475·5	482·0	451·7
87·0	503·0	510·5	477·0
87·5	530·5	540·5	506·5
88·0	560·0	571·6	538·6
88·5	590·0	604·7	571·5
89·0	621·5	639·9	608·8
89·5	653·6	676·6	646·5
90·0	687·5	714·2	685·0
90·5	725·5	753·2	725·5
91·0	761·5	794·0	766·0

used, by no means lowers the temperature to the true boiling-point. In order to do this, a rapid current must be passed through, and this would naturally vitiate the vapour-pressure measurements. The values of the vapour-pressures are compared in the table (p. 169). In the first column are given those calculated from my measurements; in the second and third those found by Olszewski and Estreicher. Those given as Estreicher's are obtained by giving weight to his intermediate points, as explained above.

The values of the vapour-pressures of oxygen and nitrogen were introduced into the equation r' gas $= r \times \frac{P_0}{P_n}$, but were not found to satisfy it, nor does the introduction of a constant factor improve it, as may be seen from the subjoined table, the last column of which expresses the ratio $\frac{r'}{r}\Big/\frac{P_0}{P_n}$.

T.	r'.	r.	$\frac{P_0}{P_n}$.	$\frac{r'}{r}$.	
80	·1364	·5004	·2174	·2725	1·254
82	·3089	1·090	·2240	·2832	1·264
84	·5835	1·959	·2322	·2979	1·283
86	1·092	3·505	·2388	·3116	1·305
88	2·290	7·065	·2480	·3241	1·307
90	8·806	24·97	·2560	·3525	1·377

There does not appear, therefore, to be any connexion between the ratio of the vapour-pressures and the composition of the gaseous phase in the distillation of oxygen and nitrogen at constant pressure; it would be better, however, for this purpose to investigate the distillation at constant temperature, and this it is proposed to do.

I have to express my cordial thanks to Professor Ramsay, at whose suggestion the work was begun, and who has shown great personal interest during the investigation; and especially am I indebted to Dr. F. G. Donnan for the valuable help he has given me at various times.

University College, London,
February 1900.

Discussion.

Prof. Callendar referred to the question of superheating, and stated that the constant-pressure thermometer was more sensitive than the constant-volume one for measuring low temperatures.

XV. *On the Distribution of a Gas in an Electrical Field.*

By George W. Walker, *B.A., A.R.C.Sc., Sir Isaac Newton Student in the University of Cambridge*[*].

27

This paper forms part of an essay on the kinetic theory of gases, at which I have been working for some time. the essay will not be published for some time yet; but on account of the interest of the above question it seems desirable to publish the results at which I have arrived.

For the sake of generality we shall suppose that the number of free positive atoms in unit volume is n_1, the number of free negative atoms n_2, and the number of molecules N. These are averages and do not imply that the atoms which constitute the set n_1 are the same at every instant, but that we have reached a state in which the number of molecules which disintegrate is equal to the number formed by recombination. We shall regard the molecule as consisting of a pair of atoms in contact, each of mass m and radius a, and one carrying a positive charge e, and the other a negative charge $-e$.

We consider first the case in which the gas as a whole is at rest.

Let χ be the electrical potential and R the resultant force at a point.

Then Boltzmann's extension of Maxwell's distribution law gives at once

$$n_1 = N_1\epsilon^{-he\chi}, \qquad n_2 = N_2\epsilon^{+he\chi},$$

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[*] Read March 9, 1900.

$$N = -A\int_{+1}^{-1}\epsilon^{-2eah\frac{\partial\chi}{\partial\nu}\cos\vartheta}\,\delta\cos\vartheta$$

$$= A\frac{\sinh 2eah\dfrac{\partial\chi}{\partial\nu}}{eah\dfrac{\partial\chi}{\partial\nu}},$$

where $\cos\vartheta$ is the angle which the axis of a molecule makes with the direction of R, *i. e.* $-\frac{\partial\chi}{\partial\nu}$; h is the usual constant in the kinetic theory and is inversely proportional to the temperature.

We shall first show that these distribution laws satisfy the conditions of hydrostatic equilibrium.

If p be the pressure we get

$$p = \frac{n_1}{h} + \frac{n_2}{h} + \frac{N}{h},$$

which is Dalton's law of partial pressures.

Consider for the moment that χ depends only on one coordinate, x. Then we must have

$$\frac{\partial p}{\partial x} = X,$$

where X is the bodily force acting on all the atoms and molecules in unit volume.

For the free positive atoms

$$X_1 = -en_1\frac{\partial\chi}{\partial x} = \frac{1}{h}\frac{\partial n_1}{\partial x}.$$

For the free negative atoms

$$X_2 = en_2\frac{\partial\chi}{\partial x} = \frac{1}{h}\frac{\partial n_2}{\partial x}.$$

For the molecules

$$X_3 = +A2ea\frac{\partial^2\chi}{\partial x^2}\int_{+1}^{-1}\epsilon^{-2eah\frac{\partial\chi}{\partial x}\cos\vartheta}\cos\vartheta\,\delta\cos\vartheta$$

$$= \frac{1}{h}\frac{\partial N}{\partial x}.$$

Thus the equation of hydrostatic equilibrium is identically satisfied.

Let ρ be the electrical density, then

$$\frac{\partial^2\chi}{\partial x^2} = -4\pi\rho,$$

$$\rho = en_1 - en_2 - \frac{\partial \mathrm{I}}{\partial x},$$

where I is the intensity of electrification due to the molecules. It is sufficient to retain only squares of ea in calculating I, and there is little difficulty in showing that

$$\frac{\partial \mathrm{I}}{\partial x} = -\frac{4}{3}\mathrm{N}_0 ha^2 e^2 \frac{\partial^2\chi}{\partial x^2}$$

where N_0 is the number of molecules in unit volume at a part of the field where $\frac{\partial\chi}{\partial z}$ is zero.

Hence

$$\frac{\partial^2\chi}{\partial x^2} = 4\pi e(\mathrm{N}_2\epsilon^{eh\chi} - \mathrm{N}_1\epsilon^{-he\chi}) - \frac{16\pi}{3}\mathrm{N}_0 ha^2 e^2 \frac{\partial^2\chi}{\partial x^2}.$$

In general the equation is

$$\left(1 + \frac{16\pi}{3}\mathrm{N}_0 ha^2 e^2\right)\nabla^2\chi = 4\pi e(\mathrm{N}_2\epsilon^{eh\chi} - \mathrm{N}_1\epsilon^{-eh\chi}).$$

We see that the effect of the molecules is simply to increase the specific inductive capacity, so that

$$\mathrm{K} = 1 + \frac{16\pi}{3}\mathrm{N}_0 ha^2 e^2.$$

I do not propose to discuss this value of K here. Suffice it to say that with the usual estimates of $\mathrm{N}_0 h$ and a it gives very nearly Professor J. J. Thomson's value of e calculated from the electrochemical equivalent. K for a gas is, however, so nearly 1 that we may take it as 1 without vitiating our results.

The equation for χ is then

$$\nabla^2\chi = 4\pi e(\mathrm{N}_2\epsilon^{eh\chi} - \mathrm{N}_1\epsilon^{-eh\chi}).$$

In this general form little can be done with the equation; but when χ depends only on x we can obtain the complete integral

$$\frac{\partial^2\chi}{\partial x^2} = 4\pi e(\mathrm{N}_2\epsilon^{eh\chi} - \mathrm{N}_1\epsilon^{-eh\chi}).$$

Multiply by $\frac{\partial \chi}{\partial x}$ and integrate,

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h}\left\{ N_2 \epsilon^{eh\chi} + N_1 \epsilon^{-eh\chi} - B \right\}$$

where B is an arbitrary constant.

This may be rewritten

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h}\sqrt{N_1 N_2}\left\{ 2 \cosh\,(eh\chi + \alpha) - \frac{B}{\sqrt{N_1 N_2}} \right\},$$

where $$\epsilon^{2\alpha} = \frac{N_2}{N_1}.$$

Put $$\cosh\left(\frac{eh\chi+\alpha}{2}\right) = y,$$

and we get

$$\left(\frac{dy}{dx}\right)^2 = 2\pi h e^2 \sqrt{N_1 N_2}\{1 - y^2\}\left\{2 + \frac{B}{\sqrt{N_1 N_2}} - 4y^2\right\}.$$

Thus $$\cosh \frac{eh\chi + \alpha}{2} = \mathrm{sn}\,(\lambda x + \beta, k)$$

where $$\lambda^2 = 2\pi h e^2 \sqrt{N_1 N_2}\left\{2 + \frac{B}{\sqrt{N_1 N_2}}\right\}$$

$$k^2 = \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}}, \quad \text{if} \quad \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}} < 1,$$

and β is an arbitrary constant.

If $$\frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}} \quad \text{is} > 1,$$

we get

$$\cosh \frac{eh\chi + \alpha}{2} = \frac{1}{\mathrm{sn}\,(\lambda x + \beta, k)};$$

where $$\lambda^2 = 8\pi h e^2 \sqrt{N_1 N_2},$$

$$k^2 = \frac{2 + \frac{B}{\sqrt{N_1 N_2}}.}{4}$$

Before discussing the nature of the solution we shall consider the case when an electric current is passing. We shall suppose that the current is due to the bodily transference of the free atoms, while the molecules have practically no bodily motion.

Fixing our attention for the moment on the positive group :—

Let p_1 be the pressure, ρ_1 the density, so that $p_1 = \frac{\rho_1}{hm}$, and let u_1 be the group velocity. Then the hydrodynamical equations are

$$\frac{\partial u_1}{\partial t} + u_1 \frac{\partial u_1}{\partial x} = -\frac{1}{hm}\frac{\partial \log \rho_1}{\partial x} - \frac{e}{m}\frac{\partial \chi}{\partial x}$$

and

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial}{\partial x}\rho_1 u_1 = 0.$$

For a steady state

$$\frac{\partial \rho_1}{\partial t} = 0 = \frac{\partial u_1}{\partial t}.$$

Hence

$$\rho_1 = m\mathrm{N}_1 \epsilon^{-h\frac{mu_1^2}{2} - eh\chi}$$

and

$$\rho_1 u_1 = \mathrm{B}_1,$$

where N_1 and B_1 are constants.

Similarly for the negative atoms we have

$$\rho_2 = m\mathrm{N}_2 \epsilon^{-h\frac{mu_2^2}{2} + he\chi},$$

$$\rho_2 u_2 = \mathrm{B}_2.$$

Hence the electrical density at a point is

$$\frac{e}{m}(\rho_1 - \rho_2),$$

and the electrical current is

$$= \frac{e}{m}(\rho_1 u_1 - \rho_2 u_2) = \frac{e}{m}(\mathrm{B}_1 - \mathrm{B}_2) = \gamma \text{ say.}$$

If the group velocities are small compared with v_0 the velocity of light the potential is given by

$$\mathrm{K}\frac{\partial^2 \chi}{\partial x^2} = -4\pi \frac{e}{m}(\rho_1 - \rho_2).$$

Now u_1 and u_2 may be small compared with $\frac{1}{\sqrt{hm}}$, *i. e.* small compared with the velocity of sound, and still give large currents.

If this is so we have approximately

$$\rho_1 = m\mathrm{N}_1\epsilon^{-eh\chi}\left\{1 - \frac{hm}{2}\frac{\mathrm{B}_1{}^2}{\mathrm{N}_1{}^2m^2}\epsilon^{2eh\chi}\right\},$$

$$\rho_2 = m\mathrm{N}_2\epsilon^{eh\chi}\left\{1 \quad \frac{hm}{2}\frac{\mathrm{B}_2{}^2}{\mathrm{N}_2{}^2m^2}\epsilon^{-2eh\chi}\right\}.$$

Thus, taking K as 1,

$$\frac{\partial^2\chi}{\partial x^2} = 4\pi e\left\{\left(\mathrm{N}_2 + \frac{h}{2}\frac{\mathrm{B}_1{}^2}{m\mathrm{N}_1}\right)\epsilon^{+eh\chi} - \left(\mathrm{N}_1 + \frac{h}{2}\frac{\mathrm{B}_2{}^2}{m\mathrm{N}_2}\right)\epsilon^{-eh\chi}\right\},$$

which is an equation of the same form as before.

The solution is thus

$$\cosh\frac{eh\chi+\alpha}{2} = \frac{1}{\mathrm{sn}\,(\lambda x+\beta, k)}$$

where

$$\epsilon^{2\alpha} = \frac{\mathrm{N}_2 + \dfrac{h}{2m}\dfrac{\mathrm{B}_1{}^2}{\mathrm{N}_1}}{\mathrm{N}_1 + \dfrac{h}{2m}\dfrac{\mathrm{B}_2{}^2}{\mathrm{N}_2}},$$

$$\lambda^2 = 8\pi he^2\sqrt{\mathrm{N}_1\mathrm{N}_2\left(1 + \frac{h}{2m}\frac{\mathrm{B}_1{}^2}{\mathrm{N}_1\mathrm{N}_2}\right)\left(1 + \frac{h}{2m}\frac{\mathrm{B}_2{}^2}{\mathrm{N}_1\mathrm{N}_2}\right)},$$

$$k^2 = \frac{2 + \dfrac{\mathrm{B}}{\sqrt{\mathrm{N}_1\mathrm{N}_2\left(1 + \dfrac{h}{2m}\dfrac{\mathrm{B}_1{}^2}{\mathrm{N}_1\mathrm{N}_2}\right)\left(1 + \dfrac{h}{2m}\dfrac{\mathrm{B}_2{}^2}{\mathrm{N}_1\mathrm{N}_2}\right)}}}{4}.$$

The particular form of solution adopted depends on the values of the arbitrary constants introduced. When there is no potential and no current we have $\mathrm{N}_2 = \mathrm{N}_1$. Again, if we assert the condition that the total number of atoms, viz. $(\mathrm{N}_2 + \mathrm{N}_1 + 2\mathrm{N}_0) \times$ (vol.) is constant, we may regard N_2, N_1, and N_0 as known.

Since the current is made up of two streams we cannot determine B_1 and B_2 uniquely unless we impose some relation between B_1 and B_2. The most likely seems $\mathrm{B}_1 = -\mathrm{B}_2$. If the potential is given at two points then β and B are determined.

For the general discussion of the solution we may then take the form

$$\cosh\frac{eh\chi+\alpha}{2} = \operatorname{sn}(\lambda x+\beta, k),$$

where α, λ, β, k are supposed known. We get

$$\cosh eh\chi+\alpha = 2\operatorname{sn}^2(\lambda x+\beta, k)-1.$$

Now $\cosh eh\chi+\alpha$ is proportional to the matter density of free atoms. Further the density of the molecules is a function of $\left(\frac{\partial\chi}{\partial x}\right)^2$, and the first integral is

$$\left(\frac{\partial\chi}{\partial x}\right)^2 = \frac{8\pi}{h}\sqrt{N_1N_2\left\{1+\frac{h}{2m}\frac{B_1^2}{N_1N_2}\right\}\left\{1+\frac{h}{2m}\frac{B_2^2}{N_1N_2}\right\}}$$

$$\times\left\{2\cosh eh\chi+\alpha-\frac{B}{\sqrt{N_1N_2\left(1+\frac{h}{2m}\frac{B_1^2}{N_1N_2}\right)\left(1+\frac{h}{2m}\frac{B_2^2}{N_1N_2}\right)}}\right\}.$$

Thus in general the matter density of the gas is periodic. The distance between points of equal density is given by d where

$$\lambda d = m\omega + m'\omega',$$

where ω and ω' are the complete periods of the elliptic functions and m and m' are the least integers which make d real.

Sinh $eh\chi+a$, which is proportional to the electrical density, is also periodic in the same period. Where the function $\sinh eh\chi+a$ vanishes we have an equal number of free positive and negative atoms. At such a place there is most chance of recombination. It is probable that such recombination gives rise to luminosity. If the points of maximum matter density coincide with the points of least electrical density, then the above calculation would indicate that we should have very well defined planes of maximum luminosity.

The planes of minimum electrical and maximum matter density will not, however, in general coincide. Thus, though we should still have planes of maximum luminosity, they will not be so well defined.

These considerations suggest that we have something very closely related to the condition of things in a striated vacuum-tube.

In order to test this further, let us consider how the distance between these maxima planes varies as the constant B varies.

Suppose $N_1 = N_2$, and $B_1 = -B_2$,

so that the current

$$\gamma = \frac{2e}{m} B_1.$$

Our first integral takes the form

$$\left(\frac{\partial\chi}{\partial x}\right)^2 = \frac{8\pi}{h} N_1 \left\{1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right\} \left\{2\cosh eh\chi - \frac{B}{\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right) N_1}\right\}.$$

The least value which cosh $eh\chi$ can have is 1.

Suppose F the value of $\frac{\partial\chi}{\partial x}$ where $\chi = 0$.

$$\therefore \quad \frac{-B}{1 + \left(\frac{h}{2m}\frac{B_1^2}{N_1^2}\right) N_1} = \frac{hF^2}{8\pi N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right)} - 2,$$

so that

$$2 + \frac{B}{N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right)} = 4 - \frac{hF^2}{8\pi N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right)}.$$

When $F = 0$ the appropriate solution is

$$\cosh\frac{eh\chi}{2} = \coth \lambda x + \beta$$

where

$$\lambda^2 = 8\pi h e^2 N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right).$$

Here the distance d is infinite.

As F^2 increases from 0 to $\frac{32\pi N_1}{h}\left\{1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right\}$

the proper form is

$$\cosh\frac{eh\chi}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)},$$

where

$$\lambda^2 = 8\pi h e^2 N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right),$$

$$\frac{4 - \frac{hF^2}{8\pi N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right)}}{4} = 1 - \frac{hF^2}{32\pi N_1\left(1 + \frac{h}{2m}\frac{N_1^2}{B_1^2}\right)};$$

$$\therefore \qquad k'^2 = \frac{hF^2}{32\pi N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right)}.$$

For small values of k'

$$d = \frac{1}{\lambda} 2 \log \frac{4}{k'},$$

when $F^2 = \frac{32\pi N_1}{h}\left\{1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right\}$

$$\cosh \frac{eh\chi}{2} = \frac{1}{\sin \lambda x + \beta} \text{ (ordinary circular functions).}$$

$$\lambda^2 = 8\pi h e^2 N_1\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right),$$

and

$$d = \frac{\pi}{\lambda}. \quad \text{(This is the least value of } d.\text{)}$$

From

$$F^2 = \frac{32\pi N_1}{h}\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right) \text{ to } \infty$$

we get

$$\cosh \frac{eh\chi}{2} = \frac{1}{k'}\,\frac{dn\lambda x + \beta, k}{\operatorname{sn} \lambda x + \beta, k},$$

where

$$\lambda^2 = 8\pi h e^2 N_1\left\{1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right\}k'^2$$

and

$$k^2 = 1 - \frac{32\pi N_1}{h}\,\frac{\left\{1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right\}}{F^2}$$

$$k'^2 = \frac{32\pi N_1}{h}\,\frac{\left\{1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right\}}{F^2}$$

and if k' is small,

$$d = \frac{1 \times F}{16\pi N_1 e\left(1 + \frac{h}{2m}\frac{B_1^2}{N_1^2}\right)} 2 \log \frac{4}{k'}.$$

Now Goldstein (Wied. *Ann.* xv. p. 277, 1883) finds that d is very nearly inversely proportional to the density, while Mr. R. S. Willoughs (Cav. Lab.) finds that above a certain strength of current the distance d diminishes as the current increases. N_1 will be proportional to the density multiplied by some function of F, so that the formula for d will agree fairly well with these experimental results if F^2 lies between $\frac{32\pi N_1}{h}\left\{1+\frac{h}{2m}\frac{B_1^2}{N_1^2}\right\}$ and ∞.

The distance between the striæ depends on the diameter of the discharge-tube. It is possible that the solution of the general differential equation for χ would lead to this, but it seems hopeless to attack the equation for two dimensions.

Another interesting deduction from the solution above, which has been verified experimentally since I made the calculation, is that while $\frac{\partial \chi}{\partial x}$ is periodic in the striæ the potential χ is not periodic.

The equation $\cosh\frac{eh\chi+\alpha}{2}=\text{sn}\,(\lambda x+\beta,\, k)$ may be transformed into

$$\sin\psi=\mu\,\text{sn}\,(v, k)^*,$$

where ψ is a linear function of χ,
v „ „ „ x,
μ some constant,
k some modulus.

Now this equation is just of the same form as that for the motion of a simple pendulum under gravity, ψ being the angle, and v the time, and we know that when the pendulum makes complete revolutions it is possible to express ψ as equal to μv and a series of periodic terms.

Thus, χ in general is a linear function of x and a series of periodic terms.

χ must be real, and the series convergent. This will

---

* In the equation $\frac{\partial^2\chi}{\partial x^2}=8\pi e\sqrt{N_1N_2}\sinh\,(eh\chi+\alpha)$ put

$$eh\chi+\alpha=i\psi,$$
$$x=it$$

and we get
$$\frac{\partial^2\psi}{\partial t^2}=-8\pi e^2h\sqrt{N_1N_2}\sin\psi,$$

which is the equation of motion of a simple pendulum.

depend on the particular circumstances. That the series must converge to zero in one case is obvious, for if there are no free atoms $\chi = Ax + B$ is a complete solution of the equation.

Further, $\frac{\partial \chi}{\partial x}$ is periodic, although χ is not so.

I understand that from measurements of χ in the striæ, χ is just of the nature we have found, while Mr. H. A. Wilson, at the Cavendish Laboratory, finds that $\frac{\partial \chi}{\partial x}$ is periodic.

XVI. *On the Damping of Galvanometer-Needles. By* Maurice Solomon[*]. (Communicated by Prof. Ayrton, F.R.S.)

It is well known that shortening the period of oscillation of a galvanometer-needle by increasing the strength of the magnetic controlling field decreases the *decrement*, or ratio of one complete swing to the next. It follows therefore that for a given initial amplitude of vibration a needle swinging in a strong controlling field will make a greater number of oscillations before coming to rest than when swinging in a weak field; but since the time of each oscillation is less in the former case it does not follow that the time required for the amplitude to be reduced to a given fraction $\left(\text{say } \frac{1}{m}\right)$ of its initial value is greater with a strong than with a weak controlling field.

Examining the question theoretically, and making the usual assumption that the retarding forces are proportional to the first power of the velocity, one arrives at the conclusion that the time taken for the amplitude to become $1/m$ of its initial value is independent of the strength of the controlling field, and so the time taken by the needle in coming to rest from a given initial deflexion should be the same whether the period of vibration is long or short.

For, making the assumption stated above, we have as the equation of motion for a needle of magnetic moment M, and of moment of inertia I, swinging in a uniform magnetic field of strength H,

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[*] Read March 9, 1900.

$$I\frac{d^2\alpha}{dt^2}+N\frac{d\alpha}{dt}+HM\sin\alpha=0,$$

where α is the deflexion at time t, and N is the coefficient allowing for the *damping*, by which is meant *the resistance tending to destroy the motion of the needle.* This resistance is due to the viscosity of the air and of the suspension fibre, and also to the eddy-currents set up by the swinging needle in neighbouring metallic circuits. Of these retarding forces that due to the eddy-currents must be proportional to the first power of the velocity; but it is possible that those due to the viscosity of the air and the suspension fibre vary as some function of the velocity other than its first power.

When the angle of swing is small we may take α instead of sin α, and if we put

$$N/I=2n,$$

and

$$HM/I=p^2,$$

the above equation becomes

$$\frac{d^2\alpha}{dt^2}+2n\frac{d\alpha}{dt}+p^2\alpha=0.$$

This equation can easily be solved and gives for the periodic time reckoned either from one maximum deflexion to the next maximum deflexion on the same side, or, as the time between two successive crossings of the zero in the same direction,

$$t=\frac{2\pi}{\sqrt{p^2-n^2}},$$

and if δ be the decrement, or ratio of one complete swing to the next, we obtain

$$\delta=e^{\frac{n\pi}{\sqrt{p^2-n^2}}},$$

so that the logarithm of the decrement to the base e, known as the *logarithmic decrement*, is

$$\lambda=\frac{n\pi}{\sqrt{p^2-n^2}}.$$

The true periodic time, T, of the swinging system, that is to say the periodic time it would have if the damping forces were absent, is given by

$$T = t\frac{\pi}{\sqrt{\pi^2+\lambda^2}}.$$

From the expressions above found for the observed periodic time t and the logarithmic decrement λ, we get

$$\frac{t}{\lambda} = \frac{2}{n} = \frac{4I}{N},$$

so that the ratio t/λ is independent of the strength H of the controlling field, and will remain constant when t is varied by altering this strength, provided I and N remain constant.

The time τ for the reduction of the deflexion to $\frac{1}{m}$ of its original value is given by

$$\tau = \tfrac{1}{2}\log_e m \frac{t}{\lambda},$$

and is therefore constant so long as t/λ is constant, or, consequently, so long as I and N remain constant.

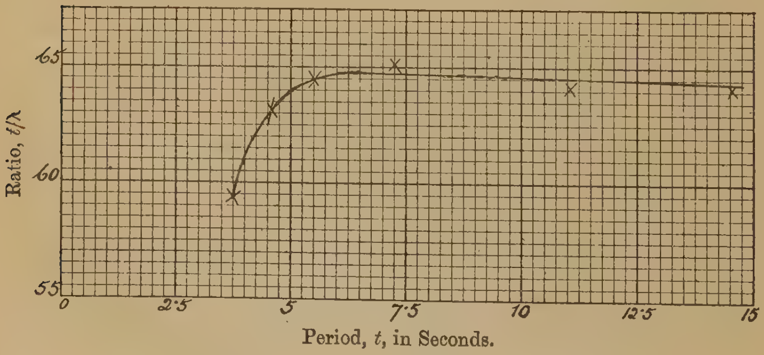
With a view to testing the conclusion arrived at by the above reasoning, experiments have been made at the Central Technical College, beginning in 1891 and continued at intervals since that time, the results of which have shown a decided discrepancy between theory and experiment. The method adopted was to observe the periodic time and the corresponding decrement with different strengths of controlling field. Calculating out from these observations the values of the ratio t/λ, i.e. the ratio of the periodic time to the logarithmic decrement, showed that in most of the instruments tested the value of this ratio was not constant as indicated by theory. As examples of the results obtained, three sets of experiments on galvanometers of different types may be quoted.

The first set of experiments was made by Mr. Seaman in 1891, on a Mudford's Thomson galvanometer similar to that illustrated in fig. 6 of Messrs. Ayrton, Mather, and Sumpner's paper on "Galvanometers" (Phil. Mag. July 1890, p. 70). The suspended system consists of an aluminium wire having small magnets affixed to the upper and lower ends, and the mirror affixed at the centre. The mirror is enclosed in a small case with glass back and front so arranged that these glasses can be screwed nearer together or farther apart, thus enabling the space in which the mirror swings, and consequently the air damping, to be varied. A pair of coils is placed one behind and one before the upper set of magnets, and a similar pair before and behind the lower set, the coils being enclosed in ebonite boxes fitted into a brass frame. By thus placing the mirror outside, instead of at the centre of the coils, an improvement introduced into the Thomson galvanometer by Mr. Mudford, the coils may be wound practically to the centre and much valuable space utilized. The strength of the controlling field is varied by sliding a magnet up and down a vertical upright fixed to the top of the instrument case. As a result of these experiments Mr. Seaman found that the ratio t/λ increased as the period increased, becoming, however, nearly constant at long periods. The actual results are given in Table I., and plotted as a curve in fig. 1. This curve is plotted with the values of t, the observed period, as abscissæ, and the values of t/λ as ordinates, the values of t/λ being taken in preference to those of λ/t, as might appear more rational, because, as has been shown

TABLE I.—Mudford's Thomson Galvanometer.

Period, t, in seconds ……	3·75	4·63	5·46	7·24	11·06	14·55
Logarithmic decrement, λ	0·0631	0·0734	0·0854	0·1112	0·1725	0·2268
Ratio, t/λ ………………	59·4	63·2	64·5	65·1	64·2	64·1

Fig. 1.



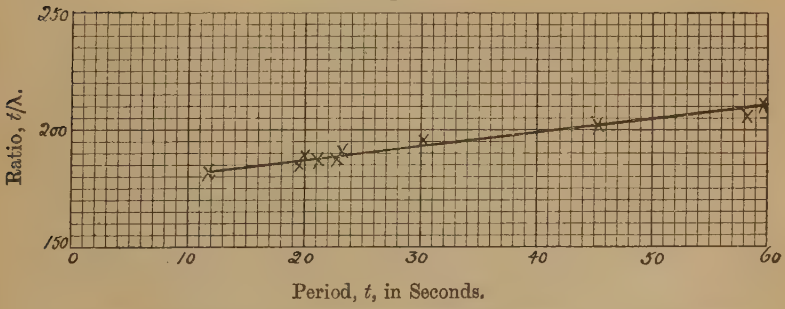
above, it is the ratio t/λ that occurs in the expression for the time of the reduction of the deflexion to $1/m$ of its original value.

A series of experiments was made by Mr. Macquay in 1896 on a ballistic galvanometer, made by Messrs. White of Glasgow to the designs of Messrs. T. & A. Gray, which is illustrated in figs. 11 and 12 of the paper above referred to. In this instrument there are a pair of long needles arranged to form an astatic combination, and each having one end sucked into and the other end pushed out of a coil, the four coils being enclosed in rectangular ebonite boxes. These needles are attached by an aluminium bridge to a vertical aluminium wire fastened at its upper end to the suspending fibre, and carrying at its lower end a pair of mirrors fastened back to back, the one being concave and the other plane, and also carrying at its lower end a small magnetic needle between a pair of auxiliary coils intended to be joined up in series with a battery and reversing-key and used as damping coils. The strength of the controlling field is varied by moving a magnet placed on the bench on which the instrument stands up to or away from the galvanometer. The results obtained showed a decided steady increase in the ratio t/λ with an increase of t. (See Table II. fig. 2.)

TABLE II.—Ballistic Galvanometer.

Period, t, in seconds ...	11·8	19·6	20·0	21·1	22·9	23·1	30·1	45·6	58·2	59·7
Logarithmic decrement, λ	0·0654	0·106	0·106	0·113	0·122	0·121	0·154	0·227	0·283	0·284
Ratio, t/λ.........	180·8	185·0	188·6	186·8	187·0	190·8	195·3	200·6	205·5	210·3

Fig. 2.

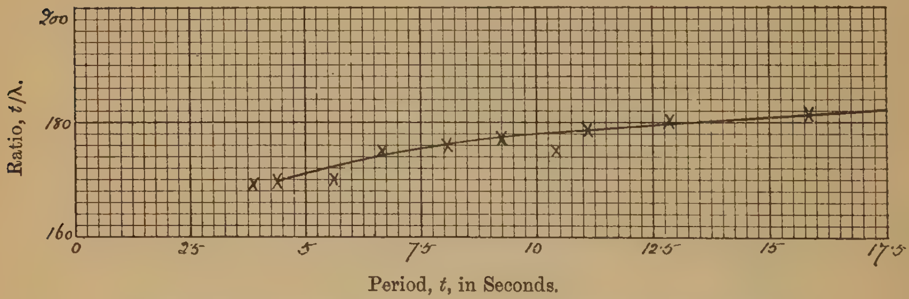


Finally, Mr. Taylor made some experiments in 1896 upon a Rosenthal galvanometer. The suspended system of this instrument is illustrated in fig. 10 of the paper previously referred to, and consists of an astatic pair of needles fastened below the mirror, each needle being bent into the shape of a horseshoe. One pole of each needle passes into the centre of a coil, whilst the other pole is on the outside of the coil, and the needles are therefore sucked into or pushed out of these coils by the action of the current. The results of these experiments showed an increase in the ratio t/λ as t increased, the change being slightly more marked at the short periods. (See Table III. and fig. 3.)

TABLE III.—Rosenthal Galvanometer.

Period, t, in seconds ...	3·86	4·33	5·61	6·70	8·10	9·25	10·40	11·08	12·80	15·80	18·60
Logarithmic decrement, λ	0·0228	0·0256	0·0330	0·0382	0·0459	0·0523	0·0597	0·0618	0·0709	0·0873	0·113
Ratio, t/λ... ..	169·5	169·3	170	175	176	177	175	179	180·5	181	182·5

Fig. 3.



These experiments (which have been selected from amongst the large number made at the Central Technical College as being typical) succeed in establishing the fact that the ratio t/λ does not remain constant when the strength of the controlling field is altered, but they do not explain why the conclusion derived from the theoretical equation is not borne out in practice. At the suggestion of Mr. Mather I made a series of experiments to find out if possible to what cause the variation in the ratio was due. It has been shown above that the ratio t/λ will remain constant when the strength of the controlling field is varied, provided that I and N remain constant. N, it is to be noticed, allows for the damping caused by the viscosity of the air and the suspension, and by the eddy-currents, and is therefore so far as the last cause is concerned a function of M, the magnetic moment of the swinging needle, and consequently will not remain constant if the strength of the controlling field affects the strength of the needle. We have then the following possible explanations of the variation of the ratio :—

1. I *may not be constant.*—This may occur through the controlling magnet deflecting the swinging system slightly from the vertical, and thus altering the axis of rotation : this is more likely to occur when the field is varied by moving the controlling magnet in a horizontal plane than when it is varied by moving the magnet up and down in a vertical plane passing through the needle.
2. N *may not be constant.*—This may occur in three ways :—
    - i. The factor introduced by the air resistance may not be constant, the air resistance being possibly not proportional to the first power of the velocity.
    - ii. For the same reason it is possible that the factor introduced by the viscosity of the suspension may not be constant.
    - iii. The factor introduced by the eddy-current damping may not be constant. There are three causes which may make this factor vary.

In the first place, since the E.M.F. induced by the swinging needle is proportional to the first power of its velocity and to its strength, the damping effect of the eddy-currents will be proportional to the square of the strength of the swinging needle ; and it is quite possible that altering the strength of the controlling field may alter the strength of the needle.

Secondly, if the galvanometer coils have a self-induction such that the reactance is not negligible, at the periods used, when compared with the resistance, the eddy-currents set up will not only lag behind the induced E.M.F., but will be to a certain extent choked out. And as these effects will be greater during the fast periods, the damping will be diminished for these periods, thus causing the ratio t/λ *to increase as the period decreases.*

Thirdly, it is possible that the eddy-currents will produce a rise in temperature sufficient to appreciably affect the resistance of the galvanometer coils. This will diminish the eddy-currents most at the short periods, thus producing an effect similar to that due to self-induction, namely *an increase of* t/λ *as the period decreases.*

To find out if possible which of the above was the true cause of the discrepancy between theory and experiment, it was decided to make some experiments in which the ratio t/λ was first determined for various strengths of controlling field for a needle swinging in a system in which the eddy-current damping was reduced to a minimum, if not entirely eliminated: and secondly for the same system but with considerable eddy-current damping introduced. In this way it would be possible to discover whether the effect was due to the eddy-currents or not.

Some preliminary trials showed that, to obtain satisfactory observations with vibrations of long period, it would be necessary to perform the experiments at night when there was comparative freedom from the disturbances due to traffic, since, although the galvanometer was placed on a stone foundation-pillar, it was found impossible to get good readings when the traffic was at all frequent. The whole set of observations was therefore made between twelve and six on the morning of June 23rd, 1898. A sixty-ohm simple reflecting galvanometer was used with an astatic combination of four small needles affixed to a wire to the upper end of which the mirror was fastened, the whole being suspended by a single silk fibre. This system swung between the coils of the galvanometer, and as it had no mica vane the air damping was not great. As the coils were of fine wire, and the parts of the galvanometer nearly all of wood, the eddy-currents would be very small when the coils were on open circuit, and the damping in that case would be almost entirely due to the air resistance and the viscosity of the suspension. When, however, the galvanometer circuit was closed by short-circuiting the terminals, eddy-currents would be set up, and would introduce a considerable factor in the damping; so that if the alteration in the ratio t/λ is due to the factor introduced by the eddy-currents, it would be observable with the galvanometer circuit closed, but not with it open.

The determinations of the period were made by observing with a stop watch the time taken in executing several complete swings—from five or six when the period was long, to twenty when it was short. The time was read as the spot of light passed the zero of the galvanometer scale. Unfortunately in the experiments with a period of 16 seconds the true zero was about 25 divisions out, in such a direction as to cause the observed period to be too small. Had the amplitudes of the first and last swings used in determining the period been observed, it would be possible to make an accurate correction: as this was not done, it is only possible to make an approximate one, which will not, however, be far wrong, and which has been made in the results given in the table.

In observing the decrement when the period was long, the amplitudes of successive swings on both sides of the zero were observed. If these be a, b, c, d, e, . . . &c., we have

$$\text{Decrement} = \frac{a}{b} = \frac{b}{c} = \ldots = \frac{a+b}{b+c} = \frac{b+c}{c+d} = \ldots \text{\&c.}$$

By thus using $\frac{a+b}{b+c}$ instead of $\frac{a}{b}$ to calculate the decrement any zero error is eliminated. A specimen of the actual readings obtained in an observation of this type is appended.

Galvanometer-Circuit closed. Period 7·78 seconds.

Decrement—

(*a*) $\frac{543}{482}=1{\cdot}126,\quad \frac{482}{431}=1{\cdot}119,\quad \frac{431}{383}=1{\cdot}126,\quad \frac{383}{341}=1{\cdot}122,$

$\frac{341}{305}=1{\cdot}117,\quad \frac{305}{272}=1{\cdot}121,\quad \frac{272}{242}=1{\cdot}125,\quad \frac{242}{217}=1{\cdot}115,\quad \frac{217}{193}=1{\cdot}125.$

(*b*) $\frac{566}{504}=1{\cdot}124,\quad \frac{504}{450}=1{\cdot}119,\quad \frac{450}{399}=1{\cdot}127,\quad \frac{399}{357}=1{\cdot}118,$

$\frac{357}{319}=1{\cdot}120,\quad \frac{319}{284}=1{\cdot}122,\quad \frac{284}{254}=1{\cdot}116,\quad \frac{254}{226}=1{\cdot}124,\quad \frac{226}{201}=1{\cdot}125.$

Mean of above values$=1{\cdot}121$.

Average decrement from observations (*a*) $= \sqrt[9]{\frac{543}{193}} = 1{\cdot}120.$

" " " " (*b*) $= \sqrt[9]{\frac{566}{201}} = 1{\cdot}122.$

Mean decrement, $\delta = 1{\cdot}121.$
$\lambda = \log_e \delta = 0{\cdot}114.$
Ratio, $t/\lambda = 68{\cdot}1.$

When the period was short, the spot of light moved too quickly for me to be able to read on both sides of the zero. For the two cases in which the period was 2·66 and 3·65 seconds respectively, I accordingly observed successive swings on the same side of the zero. We then have

$$\frac{a}{c} = \frac{a}{b} \cdot \frac{b}{c} = \delta^2.$$

Hence the values for λ are hardly so certain in these cases as in those in which the period was longer, especially as the spot of light moves so fast that it is more difficult to observe the deflexions accurately. A specimen of the readings of this type is given below.

Galvanometer-Circuit open. Period 3·65 seconds.

(Decrement)^2—

(*a*) $\frac{313}{288} = 1{\cdot}087$, $\frac{288}{262} = 1{\cdot}097$, $\frac{262}{240} = 1{\cdot}090$, $\frac{240}{218} = 1{\cdot}100$, $\frac{218}{199} = 1{\cdot}092$,
$\frac{199}{183} = 1{\cdot}090$, $\frac{183}{166} = 1{\cdot}101$, $\frac{166}{151} = 1{\cdot}099$, $\frac{151}{138} = 1{\cdot}093$, $\frac{138}{124} = 1{\cdot}112$,
$\frac{124}{114} = 1{\cdot}087$, $\frac{114}{105} = 1{\cdot}086$.

(*b*) $\frac{284}{260} = 1{\cdot}093$, $\frac{260}{237} = 1{\cdot}096$, $\frac{237}{215} = 1{\cdot}102$, $\frac{215}{198} = 1{\cdot}087$, $\frac{198}{180} = 1{\cdot}098$,
$\frac{180}{164} = 1{\cdot}096$, $\frac{164}{149} = 1{\cdot}099$, $\frac{149}{137} = 1{\cdot}088$, $\frac{137}{125} = 1{\cdot}096$, $\frac{125}{114} = 1{\cdot}096$,
$\frac{114}{104} = 1{\cdot}095$.

Square root of mean of above values $= 1{\cdot}047$.

Average decrement for observations (*a*) $= \sqrt[24]{\frac{313}{105}} = 1{\cdot}0465.$

" " " " (*b*) $= \sqrt[22]{\frac{284}{104}} = 1{\cdot}0475.$

Mean decrement, $\delta = 1{\cdot}047.$
$\lambda = \log_e \delta = 0{\cdot}0459.$
Ratio, $t/\lambda = 79{\cdot}5.$

Altogether six results were obtained for the galvanometer on open circuit, and a corresponding set for closed circuit. The experiments were made by first adjusting the controlling field until a suitable period was obtained; this was done by moving the controlling magnet, which rested on the bench on which the galvanometer stood, up to or away from the instrument. The period and decrement were then observed with the galvanometer on open circuit; the terminals of the galvanometer were then short-circuited, and a fresh observation of the period and decrement made. The initial deflexion was in all cases given to the needle by bringing a weak magnet into its neighbourhood, and the needle was started swinging by the sudden removal of this magnet. The results obtained are tabulated below (Table IV.) and plotted as a curve in fig. 4 (p. 192).

These results show that the ratio t/λ is constant for all the periods observed—from 2·5 to 16·5 seconds—when the galvanometer coils are on open circuit. When, however, the terminals are short-circuited, we see, in the first place, that the damping is increased, showing that eddy-current damping has been introduced, and secondly that the ratio t/λ is no longer constant, but increases with the period, *i. e.* with a decrease in the strength of the controlling field, becoming, however, constant at the higher periods. It is evident, therefore, that the alteration in the ratio is due to the eddy-current damping: and, moreover, of the three ways in which it has been pointed out the eddy-current damping may be affected, only the first is consistent with a decrease in the value of t/λ as the period decreases; for both the self-induction of the galvanometer-coils and change in their resistance due to a rise in temperature caused by the induced currents would cause the ratio to increase as the period decreased. *We must therefore conclude that the change in the ratio t/λ is due to an alteration in the strength of the swinging needle produced by altering the strength of the controlling field.*

It will be noticed that although all the experiments agree in showing that t/λ is not a constant, yet the law of its variation is different in different galvanometers. It is evident when we consider what is the cause of this variation, that this might be expected; for the law must be dependent on the

Fig. 4.

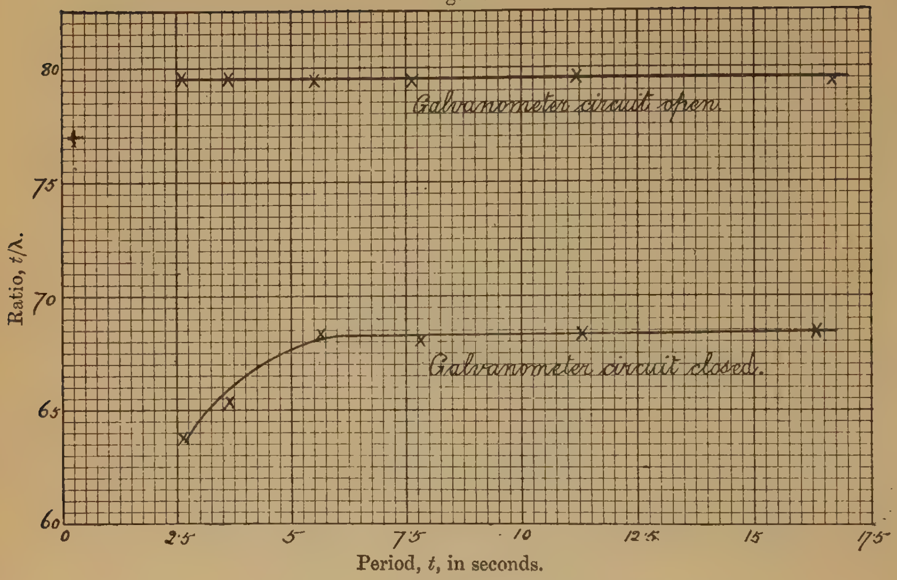


TABLE IV.

Experiment.	Observed Period $=t$.	Undamped Period $=$T,	Decrement $=\delta$.	$\text{Log}_e\,\delta=\lambda$.	Rati t/λ.
Galvanometer Circuit open.					
a	2·66	2·66	1·034	0·0344	79·6
b	3·65	3·65	1·047	0·0459	79·5
c	5·52	5·52	1·072	0·0695	79·4
d	7·64	7·635	1·101	0·0962	79·4
e	11·18	11·17	1·150	0·140	79·6
f (corrected)	16·70	16·66	1·233	0·209	79·4
Galvanometer Circuit closed.					
a	2·66	2·66	1·0425	0·0417	63·8
b	3·65	3·65	1·057	0·0560	65·3
c	5·70	5·70	1·087	0·0834	68·3
d	7·78	7·775	1·121	0·114	68·1
e	11·27	11·26	1·180	0·165	68·3
f (corrected)	16·30	16·26	1·269	0·238	68·5

construction of the galvanometer and the conditions under which it is tested. The problem is further complicated by the fact that astatic combinations are generally used. The variation in the ratio will depend upon the alteration in strength in each of the magnets of which the combination is composed: and since some of these magnets may be nearer the controlling magnet than others, they will be more affected by altering the position of the controlling magnet. It is, moreover, possible that one of the magnets in the astatic combination may be more favourably situated, by being near metal parts of the instrument, for example, for producing eddy-currents, in which case any changes in its strength will have a proportionately larger influence on the total change in the eddy-current damping. In addition, the change in the strength of any particular magnet will depend upon its initial magnetization, on the steel of which it is made, and also to a certain extent on its previous history. When we remember, further, that the percentage change in the value of the ratio t/λ depends upon how much of the damping is due to eddy-currents and how much to the other causes, viscosity of the air and the suspension, we see that we may expect the ratio to vary in a very great number of different ways.

My thanks are particularly due to Mr. T. Mather for advice as to carrying out the experiments, which were made at his and Prof. W. E. Ayrton's suggestion.

Discussion.

Mr. Blakesley said it was interesting to note the fact that the ratio of period to decrement was independent of the controlling field. In the case of a condenser discharging this ratio is independent of the capacity; in the case of a tuning-fork, of the rigidity, and in the case of water oscillating up and down in a U-tube, of the acceleration due to gravity.

Mr. Rosenbaum said that the ratio considered was constant in the case of a Nalder D'Arsonval galvanometer.

Mr. Solomon said that his arguments did not apply to galvanometers of this description because the swinging system was not a magnetic needle, but simply a coil.

XVII. *The Heat of Formation of Alloys.* *By* J. B. Tayler, *B.Sc.(Vict.), University College, Liverpool*[*]. (Communicated by Prof. Lodge, F.R.S.)

Experiments have been made upon alloys of lead with tin, bismuth, and zinc, and of zinc with tin and mercury. The method employed, which determined the choice of alloys, consists in dissolving (*a*) the alloy, and (*b*) the corresponding mixture of metals, in mercury, and measuring the heat of solution in each case. Assuming that the solutions so obtained are identical, the difference between the heat of solution of the mixture and that of the alloy is the heat of formation of the latter. The method is thus not very different in principle from that employed by Dr. Galt[†], and probably also that employed in an as yet unpublished research by Mr. Baker in the determination of the heat of formation of brass.

The calorimeter used is shown in the figure. Four were made, differing only in size and minor details. In the first two the inner vessel (*a* in the figure) was of such a size that 300 grammes of mercury could be used; the two later ones took 500 grammes. In all cases *a* was a tube of thin glass held in place in a larger and thicker tube (*b*) by an indiarubber ring. The outer tube could be similarly fitted into the bottle *c*. To reduce radiation the vessels were silvered, *a* on the outside, *b* and *c* on the inside. The calorimeter was closed by an indiarubber stopper which carried a small receptacle *d* also of glass. An elastic band projected about $\frac{1}{16}$ of an inch beyond the lower end of *d*, so forming a pad against which the wooden cone *h* could be pressed. The latter communicated by a stiff wire with the outside, and could be raised or lowered at will; when necessary, from a distance. The glass stirrer could likewise be worked, and the thermometer read, without going up to the calorimeter. These precautions were only taken in the later experiments.

The thermometer used with the first two calorimeters was graduated in tenths, and could be read to hundredths of a degree. That used subsequently was graduated in hundredths, and could be read to the one-thousandth of a degree. (The results of the two sets of experiments can be distinguished by the water-value of the calorimeter.) The experiments were

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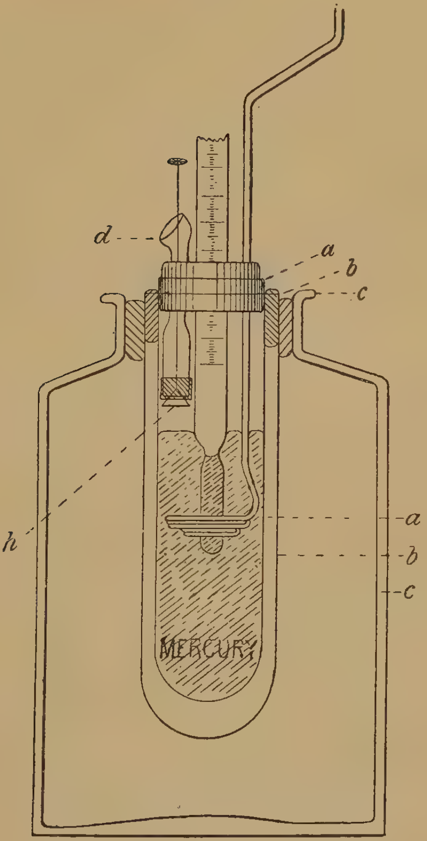
[*] Read May 11, 1900.

[†] Brit. Assoc. Rep. 1898, pp. 787, 788, and B. A. Rep. 1899.

Fig. 1.



conducted in the Chemical department of the College, and no special precautions could be taken to keep the room at constant temperature; and the thermometer was sometimes subjected to changes two or three times as large as the one to be measured, since the mercury had to be weighed in another room.

The water-values of the calorimeters were measured experimentally. This was done by running in mercury at 100° C., the operations being in all other respects precisely the same as when a heat of solution was being determined. In each case the mean of five to ten experiments was taken.

The order of procedure was the following:—The mercury in which the metal or alloy was to be dissolved was weighed into the inner vessel of the calorimeter, and the thermometer and stirrer placed in position. The alloy (or metal) was then filed, and the filings weighed and introduced into the receiver *d*. After the lapse of about a quarter of an hour the stirrer was agitated (always by hand) and the temperature read at short time-intervals. Sufficient readings having been obtained for the radiation curve, the filings were allowed to drop on to the mercury by lowering *h*, and temperature readings were taken for the next 5 to 15 minutes. Solution was often complete in less than a minute, and rarely took more than 2½ minutes.

The mercury was always purified before use by treatment with nitric acid. One-fifth of its volume of concentrated acid was poured on, and the mercury thoroughly agitated. The whole was left over-night, and the crust of nitrate broken off and removed as far as possible in the morning. The mercury was then washed with water, dried with calcium sulphate, and filtered through chamois leather. Moreover, each alloy and its corresponding mixture were always dissolved in mercury from the same batch, so that only the heat of solution, and not the heat of formation, could be affected by impurities. The metals were obtained from Kahlbaum; but some experiments with commercially pure zinc showed that small quantities of impurities did not appreciably affect the result. To make the alloys, it was found best to melt the metal of which the larger quantity was being used in a graphite crucible, and to drop the other in solid. All the metals used melt at a low temperature, and very little oxidation seems to have taken place. When a eutectic* alloy was wanted, the fluid mass was poured, after stirring, into a deep cylindrical mould maintained for some time a few degrees above the melting-point of the eutectic and then gradually cooled down. The line of demarcation between the eutectic and the upper layer was invariably sharp. The alloy A, in Table I., was formed by dissolving the requisite quantity of zinc in molten lead; B was a true eutectic. Of the alloys of lead and tin, those containing 2·0 and 5·1 per cent. of the latter were made by adding lead to the 21 per cent. alloy; as it was thought that the more nearly equal the two portions melted together, the smaller would the percentage error be. In no case was an analysis made. In order, as far as possible, to ensure homogeneity in the alloys, they were kept stirred until they had nearly cooled down to the solidifying point, and were then poured out into shallow carbon moulds. Both from their behaviour under the file and from their heat of solution, the alloys seem to have been homogeneous, with the exception of the amalgam of zinc containing 25·9 per cent. of that metal. This separated into two portions, one of which was lighter and softer than the other. The former is distinguished as α, and the latter as β, in the table of results.

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* This is Dr. Guthrie's name for the alloy with the lowest melting-point.

The alloys first experimented upon contained their constituents in equivalent proportions, and the heats of formation were found to be small in comparison with those found for brass by Dr. Galt and Mr. Baker. Since the alloys concerned belonged to the class which Matthiessen regarded as solutions, and since they were made at comparatively low temperatures, it was thought that definite chemical combination had only taken place between a small percentage of the atoms present, and that more reliable results would be obtained by dissolving small quantities of one metal in a large excess of others. The heat of formation *per gramme of alloy* was found to be higher in the cases tried; and the heat of formation of the gramme-molecular weight of *compound*, supposing that the whole of the metal present in small quantity had entered into chemical combination by the exercise of its normal valency, was, of course, immensely greater. The latter is the quantity it was desired to be sure about, the object of the work being to determine the order of magnitude of the chemical forces which effect the combination of metals. The second column of Table II. contains the figures calculated from those in the first column on the above supposition.

Incidentally it appears that the so-called "mechanical

TABLE I.

	Alloy.	Solution of Alloy.				Solution of Mixture.				Heat of Formation of 1 grm. Alloy in Calories.
		Grammes used.	Water-value of Calorimeter in Grams.	Temp. fall, °C.	Heat of Solution per grm. in Calories.	Grammes used.	Water-value of Calorimeter in Grms.	Temp. fall, ° C.	Heat of Solution per grm. in Calories.	
Lead-Zinc.	Lead-Zinc (Eutectic). Zinc 1·6 p. c. A * B *	2·26 1·308	18·9 18·3	1·06 0·557	8·9 7·8	1·293	18·4	0·988	14·1	−5·8
					8·3				14·1	
	Lead-Zinc. Zinc 23·9 p. c.	0·6542 0·704 0·975	17·0 17·3 17·4	0·350 0·470 0·550	9·1 11·3 10·0	0·878 0·867 0·840	17·3 17·3 17·4	0·69 0·64 0·70	13·6 12·8 14·5	−3·5
					10·1				13·6	
	Lead-Bismuth (Eutectic). Bismuth 44·4 p. c.	0·990	18·3	0·824	15·2	0·994	18·3	0·618	11·4	+3·8
Lead-Tin Alloys.	Lead-Tin. Tin 2·0 p. c.	1·8389 2·1839 0·9834 1·7555 1·1678	26·51 28·51 26·60 28·21 26·66	0·774 1·040 0·505 0·759 0·565	11·18 13·55 13·66 12·20 12·89	1·9377 2·2335	26·70 28·24	0·949 1·072	13·79 13·55	−1·0
					12·70				13·67	

LEAD-TIN ALLOYS.	Lead-Tin. Tin 5·1 p. c.	1·3416 1·6543 1·4686	26·62 28·28 28·47	0·713 0·662 0·687	14·1 11·3 13·3	1·3069 1·4269	26·56 28·27	0·714 0·712	13·9 14·1	−1·1
					12·9				14·0	
	Lead-Tin. Tin 5·0 p. c.	1·153 1·130 1·153	18·4 18·4 18·4	0·995 0·920 0·975	15·9 15·0 15·6	1·153 1·150	18·4 18·4	1·038 1·036	16·6 16·6	−1·1
					15·5				16·6	
	Lead-Tin. Tin 21·0 p. c.	0·947 1·8377	26·67 28·41	0·567 1·049	16·0 16·2	1·8379 1·0195 1·8669 1·8378	28·33 26·67 28·33 28·28	1·140 0·619 1·077 1·132	17·59 16·19 16·34 17·42	−0·8
					16·1				16·9	
	Lead-Tin (Eutectic) Tin 61·8 p. c.	1·00 0·995	18·3 18·4	1·47 1·45	26·9 26·8	1·019	18·25	1·39	24·9	+1·9
					26·8				24·9	
	Lead-Tin. Tin 90·0 p. c.	0·662	18·4	1·11	30·9	0·660	18·4	0·97	27·0	+3·9
Tin-Zinc (Eutectic). Zinc 8·3 p. c.		0·972 0·934	18·4 18·4	1·54 1·61	29·2 31·7	0·985 0·936	18·4 18·4	1·19 1·34	22·2 26·4	+6·1
					30·4				24·3	
Zinc-Mercury. Zinc 8·7 p. c.	....	2·611	18·4	0·700	4·93		Pure Zinc.		3·15 ↑	+1·8
Zinc-Mercury. Zinc 25·9 p. c.	.........α *	1·888	18·4	1·106	10·8	0·479	18·4	0·940	36·1 ↓	+1·5
	.........β *	1·888	18·4	1·370	13·4				9·35	+4·0

* See text.

mixtures" (so Matthiessen regarded alloys of lead and zinc) and "solutions" (lead and tin, zinc and tin) contain a small percentage of true compounds, and that eutectic alloys do not necessarily correspond to the greatest evolution of heat.

TABLE II.

ALLOY.	Heat of Formation per gramme alloy in calories.	* Heat of Formation per gramme molec. weight of compound (see text) in calories.	Volts corresponding thereto.	Observed Volta Effect in volts.	Peltier E.M.F. in volts.
Lead-Zinc Eutectic. Zinc 1·6 p. c.	−5·8	−23,800	·53	·210 (Ayrton & Perry) ·31 (Pellat)	·0008
Lead-Zinc. Zinc 23·9 p. c.	−3·5	−960	·02		
Lead-Bismuth. Lead 55·6 p. c.	+3·8	+1,400	·03	...	·017
Tin-Zinc Eutectic. Zinc 8·3 p. c.	+6·1	+4,800	·10	·281 (A. & P.) ·35 (Pellat)	·0009
Lead-Tin.					
Tin 90·0 p. c.	+3·9	+8,100	·18	·099 (A. & P.)	·00009
„ 61·8 „	+1·9	+1,000	·02	·04 scratched ·10 clean. Pellat by difference.	
„ 21·0 „	−0·8	−450	·01		
„ 5·0 „	−1·1	−2,600	·06		
„ 2·0 „	−1·0	−6,500	·14		

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* The method of calculating this column may be made clearer by an example. Take the case of the first alloy in the table. The atomic weight of zinc being 65·5, a gramme-molecular weight of it, and therefore, since it is a divalent metal, of whatever combination it forms with the lead, will be contained in $100 \div 1{\cdot}6 \times 65{\cdot}5$ grms. of the alloy quite independently of the quantity of lead "combined." Hence the heat of formation per gramme-molecular weight is $-5{\cdot}8 \times \frac{100}{1{\cdot}6} \times 65{\cdot}5$ calories.

Throughout the work I have had the privilege of Prof. Lodge's advice and supervision, and my best thanks are also due to Drs. C. A. Kohn and T. L. Bailey for their kind advice upon several matters of detail.

Discussion.

Dr. Lodge pointed out that the results obtained by Galt for an alloy which appeared to be a chemical compound were in close agreement with what would be expected from the existence of the Volta contact-force on Lord Kelvin's theory.

Mr. Tomlinson pointed out that it was impossible to use the ordinary formula for the calculation of the Volta effect from the heat of formation of alloys, unless we know exactly the chemical composition of the alloy which is produced.

Mr. W. R. Cooper said that it was difficult to see that anything could be proved by applying the Kelvin equation for E.M.F. to a metallic contact unless there is ground for believing that some particular alloy of fixed composition is always formed. There is also a further difficulty in converting heat of formation into E.M.F. in cases where the metals have different valencies, for there is no reason why one valency should be selected rather than the other.

XVIII. *On the Strength of Ductile Materials under Combined Stress.* *By* JAMES J. GUEST *. (Communicated by the Secretaries.)

CONTENTS OF ARTICLES.

1. Lack of knowledge of laws of strength.
2. Separation of the isotropic materials into ductile and brittle.
3. The yield-point in Tension Tests.
4. The yield-point, rather than the ultimate, stress the criterion of strength.
5. Variations of the ultimate and yield-point stresses: annealing.
6. The elastic limit.
7. The elastic-limit effect probably due to the existence of local yield-points.
8. The yield-point, in preference to the elastic limit, selected as the criterion of strength.
9. Torsion a case of combined stress.
10. First reason for use of thin tubes as specimens.
11. Results of previous torsion experiments.
12. Previous experiments upon the yield-point under combined stress.
13. Experiments upon ultimate strength under combined stress.
14. Theories of elastic strength under combined stress: the maximum stress theory.
15. The maximum strain theory.
16. Theorem upon the limiting values of σ.
17. The maximum strain theory not disproved by published experiments.
18. The maximum shearing-stress criterion of elastic strength.
19. Further reasons for adopting thin tubes as specimens.
20. Range of stress covered by different types of experiment.
21. Method of checking the isotropism of the material as regards yield-point stresses.
22. Objections to tubes on account of want of isotropy.
23. Objections to tubes on account of large effect of defects.
24. The system of Tests.
25. The specimens and holders.
26. The tension loads.
27. The application of torque.
28. The friction of the torsion-rigging.
29. The application of the internal pressure.
30. Measurement of the fluid pressure.
31. A new type of pressure-gauge.
32. Measurement of the distorsions.
33. A new Extensometer.

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* Read May 25, 1900.

34. Errors of extensometer.
35. A new twist-measuring apparatus.
36. Proof that the torsion-mirrors measure the twist.
37. Effect of bending.
38. As a transmission dynamometer.
39. The diametral extensometer.
40. Method of making the Tests.
41. The determination of the sectional area and thickness of the tubes.
42. Calculation of the stresses.
43. Calculation of the strains.
44. Maximum shear and slide are proportional.
45. Quantities tabulated.
46. Results of the experiments—the tests on solid bars.
47. The material and shape of tubes satisfactory.
48. The elastic limit phenomenon.
49. Yield-point stresses of the same type nearly constant throughout series on each tube.
50. The variation of the maximum stress.
51. The variation of the maximum principal strain.
52. The maximum shearing-stress or slide nearly constant.
53. Graphical presentation of variations.
54. Conclusions probable for general type of stress.
55. Effect of a volumetric stress (steel).
56. Convenient view of general type of stress.
57. The copper and brass tests, and diagrams.
58. Practical conclusions and note.

1. *Lack of knowledge of the Laws of Strength.*—From the point of view of both pure and applied science, it would be of interest to know the complete laws of the strength of materials; but although a multitude of tests have been made in certain simple modes, our knowledge of the laws of strength has been extended by few experiments exposing the material to two or more principal stresses, and thus, except in the simpler cases, the elastician is without experimental guidance as to what he should seek analytically as determining the strength of the body under consideration.

In the series of experiments herein described the materials employed have been subjected to a certain variety of simultaneous principal stresses; and the results are recorded in the hope that they will prove of service to elasticians and engineers.

The simplest, and most primitive, method of ascertaining the strength of a material is to subject a cylindrical specimen of it to a direct tension or compression, and to increase the force until the specimen breaks or collapses; the breaking-stress, thus found, being taken as the basis for calculations of the strength of all pieces of that material used in structures or machines.

As material is frequently exposed to torsion, another frequently employed test is to break a circular cylinder of material by the application of a torque, the stress so found being used in calculations for shafts, &c.

2. *Separation of the Isotropic Materials into Ductile and Brittle.*—A consideration of the form of the fractured surface in the various types of test affords some suggestions. In the case of ductile materials such as iron and steel (structural) broken by tension, the material draws out at the point of rupture and the surfaces of fracture, plane or conical, are partly or entirely inclined to the axis of the specimen at about 45°. If, however, cast iron be broken in tension, there is no evidence of drawing out, and the fracture is practically normal to the axis of the specimen. When ductile specimens are broken in torsion, the surfaces of rupture are normal to the axis; but in the case of cast iron the surface of rupture takes a curious form, one of the edges of the fracture of a circular cylindrical specimen being a helix whose angle is about 45°. Some steels of a treacherous nature exhibit a fracture partaking of the two types, part of it being normal to the axis, but part extending along the length of the specimen and having the helical edge. Under compression ductile materials ultimately give way by lateral flow; cast-iron specimens exhibit rupture-surfaces inclined to the axis at about 30°.

It will be noticed that in all cases the ductile materials exhibit rupture-surfaces coincident to a large extent with the surfaces of maximum shearing-stress, suggesting that the final action in such cases partakes of the nature of a viscous flow. Cast iron, however, under tension and torsion fractures along the surfaces across which the tension or elongation is greatest; in compression it appears to fail by a shearing action, influenced perhaps by the friction of the crystals.

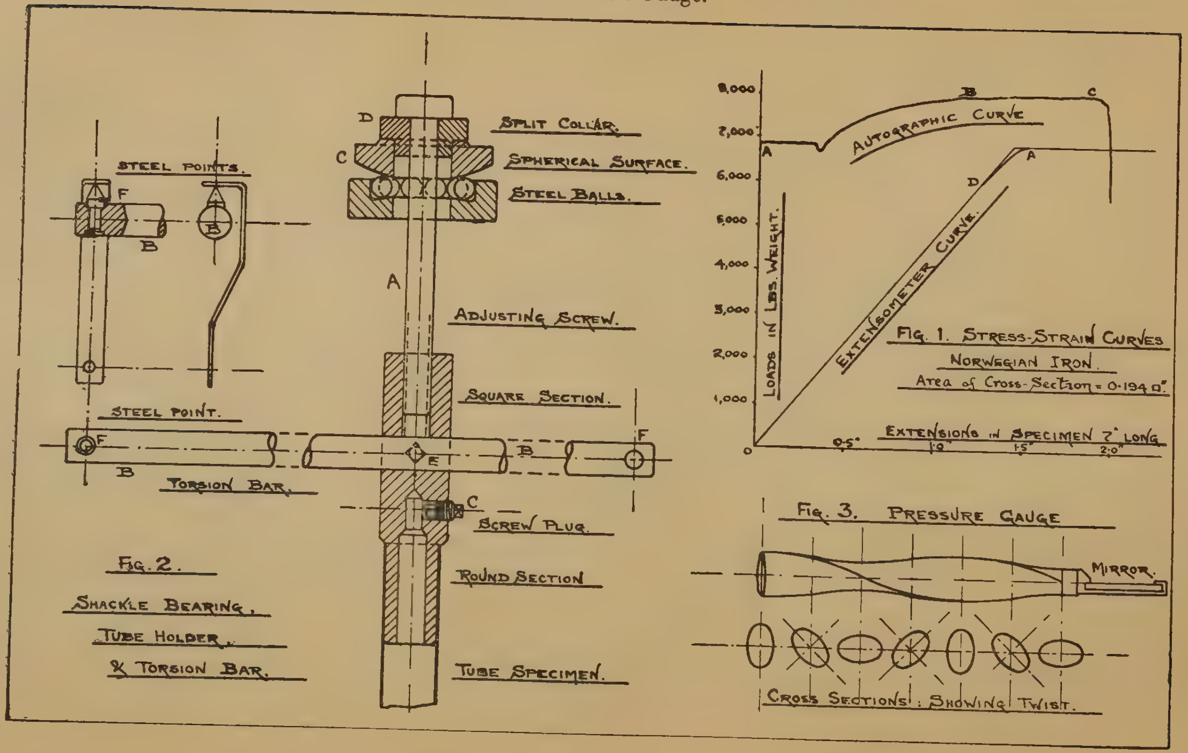
These illustrations of modes of fracture tend to show that a sharp line of demarcation may be drawn between the behaviour under stress of ductile and other materials, and this in spite of the gradual transition from one stage to the other in manufacture and in use.

Owing to the increasing tendency to substitute steel for cast iron in structures and machines, the ductile materials were selected as the subject of experiment; steel of four grades, copper, and brass have been experimented upon.

3. *The Yield-point in Tension Tests.*—Upon observing the operation of testing more carefully and taking measurements of the extension at frequent intervals, we notice that under the lower loads the specimen stretches so very slightly as hardly to affect the beam of the testing-machine. This continues until we reach a point called the yield-point, marked by a large extension of the specimen for a slight increase of load, the lever of the testing-machine in consequence moving considerably. At the same time the scale, if there is any, on the specimen peels off, starting by cracks inclined at about 45° to the generating-lines, separating the scale into squares; or if the specimen be machined, certain characteristic changes take place upon its surface. After some time the stretching under this load ceases and the load on the specimen can be increased, the elongation also increasing until rupture takes place. The loads and the measurements of the extension they produce may be plotted into a curve of which an example is shown in fig. 1, which is reproduced from a diagram (for Swedish iron) drawn automatically by a Wicksteed testing-machine, the ordinates being loads and the abscissæ actual extensions in an original length of 7 inches. Up to the yield-point the extension is very small, being about one-thousandth part of the length of the specimen; the final elongation, however, was in this case 29 per cent. of the original length.

4. *The Yield-point, rather than the ultimate, Stress the criterion of strength.*—A closer examination into the relation of the stress and strain below the yield-point shows that they are proportional to one another (Hooke's law), and it is upon this proportionality, or rather upon a generalization of which the above is a special case, that the theory of elasticity is based. Now if over any portion of a body the yield-point of the material is exceeded, the basis of our calculations is vitiated, and the redistribution of stress and strain may be widely

Fig. 1. Typical Stress-Strain Curves.
2. Testing Apparatus.
3. New Pressure Gauge.



different from the proposed distribution and lead to immediate failure. For this reason the yield-point, rather than the breaking, strength should be taken as the criterion of the strength of a ductile material in simple tension.

Further arguments to the same effect arise from Wöhler's experiments, in which he showed that the frequent repetition of a stress slightly exceeding the yield-point stress will finally cause rupture. The yield-point as the criterion of strength is so far accepted in modern practice, that most specifications of steel now call for a yield-point not lower than one half the ultimate strength.

5. *Variations of the Ultimate and Yield-point Stresses: Annealing.*—Neither the ultimate nor the yield-point stress for a material is quite definite. For the former, besides depending upon the taking account of, or the neglect of, the reduction of area due to drawing out, is affected by the rate of application of the load ; in fact, the phenomena displayed by ductile materials under stresses approaching their ultimate value are rather the dynamics of a semiviscous fluid than the statics of an elastic body. And the yield-point is affected by mechanical treatment.

If in a tension test, after the stress-strain curve has begun to rise after passing the yield-point, the load be removed, the specimen is to all appearance unchanged. Let it, however, be regarded as a new specimen and be tested : it will exhibit a yield-point close to the greatest stress previously applied to it ; but a continuance of the test will show that its capability of extension has been diminished. Such false yield-points, due to stresses or mechanical treatment, can be removed by annealing, which is generally considered to render the material isotropic.

6. *The Elastic Limit.*—It would so far appear that the yield-point is a definitely defined point with the material in its normal condition, but a closer examination of the phenomena involved brings to light a difficulty in its accurate determination. In addition to the autographic curve in fig. 1, a highly magnified edition of the same curve is shown, the points on this curve being obtained by the use of an extensometer ; the curve is referred to as the "extensometer curve." At some point D in the extensometer curve (fig. 1), before

the yield-point A, the stress-strain curve for the material ceases to be a straight line, and at the same point a time-effect manifests itself, the material yielding a little for some time after the application of the load. This time-effect renders the value of the strain just as the yield-point is reached a somewhat vague quantity; it, however, does not very materially affect the determination of the stress at the yield-point. The point at which this deviation of the straight line and time-effect appears is usually known as the elastic limit. I shall refer to the effect of time upon the strain and to the deviation of the stress-strain curve from linearity as the elastic-limit effect.

7. *The Elastic-limit effect due to the existence of Local Yield-points.*—This phenomenon may be one *sui generis*, but, partly as the departure from the straight line and the manifestation of the time-effect are simultaneous, I am inclined to think that it is due to local variations in the material, which partly by disturbing the uniform distribution of stress and strain in their neighbourhood, and partly by their nature, result in small volumes of the material reaching the yield-point prematurely, and so cause the specimen as a whole to exhibit a foreshadowing of the yield-point phenomena. On this supposition, if a specimen be once strained, as a whole, up to or beyond the yield-point, at the locations which give rise to the elastic-limit effect, the strain would be carried well beyond the yield-point; and if the load were removed, on a subsequent test they would contribute no time-effect until their new yield-point was reached, which would occur simultaneously with the yield-point of the whole specimen; hence a specimen would display no elastic-limit effect, or at any rate a very much reduced one, on a second testing. This agrees with experiment, and illustrations of it will be pointed out later. (See figs. 16, 17, & 18.)

Furthermore, although the effect is removed from a particular kind of test, it is unaffected, or even increased, for tests involving the application of stresses of a different type; examples of this may be seen in figs. 16 & 18, in which a tension and a torsion test respectively upon the material are compared, the material in the interval of the two tests having been subjected to yield-point stresses of a different type.

Not very many years ago the existence of the yield-point was not recognized, the stress-strain curve sketched as normal showing a gradual bend over (somewhat similar to the copper tension tests shown in figs. 21–24). This would be the case with imperfect material, the portions of the material in the neighbourhood of flaws and variations reaching the yield-point successively, and so masking the phenomena. There is no doubt that the materials of construction as produced to-day are much more uniform and free from defects than those of a quarter of a century ago, and thus can display phenomena perhaps hidden in the past by their imperfections.

It should be noted that the same effect (elastic-limit effect) on the stress-strain curve is caused by the non-coincidence of the axis of the specimen with the load-line.

8. *The Yield-point, in preference to the Elastic limit, selected as the criterion of strength.*—The elastic-limit effect may then be merely due to local yielding, and taking this view of it I have regarded the yield-point as the true criterion of the strength of the material, and sometimes have assumed that Hooke's law held up to it.

In all those of the experiments of this series which were made upon steel, a yield-point, sometimes much obscured by elastic-limit phenomena, was sought for and determined; and evidence will be given to show that, although there is on the whole a slight tendency for an annealed specimen, when frequently stressed, to have its yield-point rise, yet, if the material be not much strained at the yield-points, this rise is not very large, especially if the type of stress be varied. In the case of copper, the curves obtained were such as to make it difficult to determine the yield-point, if indeed one exists; several of the curves, however, have been plotted out so that the range of choice may be appreciated.

9. *Torsion, a case of Combined Stress.*—The case of torsion presents a case of combined stresses, two principal stresses being equal in amount but opposite in sign, while the third is zero. Of such tests a large number have been made on round bars, but the essentials of the phenomena involved are masked by the variation of strain from the axis outwards, which causes the outer layers to reach the yield-point first, and so produce effects corresponding to the explanation above

given of the elastic-limit effect in simple tension. As any defects in the material will contribute their effect, the result is that it is practically impossible to select the yield-point, or to determine with any degree of precision the point where the curve first deviates from the straight line.

10. *First reason for use of Thin Tubes as specimens.*—To avoid this masking of the phenomena, I conducted my experiments upon thin tubes, the walls of which were from $\frac{1}{20}$ to $\frac{1}{25}$ of the radius in thickness. I also tested two solid bars, more to ascertain, from the agreement of the elastic constants with their known values, that no large mistake had been made in the measurement of the parts of the apparatus. An inspection of the torsion stress-strain, or rather torque-twist curves (fig. 15), for these bars will show the practical impossibility of locating the yield-point (or the elastic-limit, if it be a true phenomenon), particularly if we bear in mind Mr. Love's theorem that a small round flaw will double the shearing-stress in its neighbourhood, which if the flaw were near the surface would produce the elastic-limit effect at about half the true yield-point torque.

11. *Results of previous Torsion Experiments.*—Published results of torsion experiments (see Unwin, 'Machine Design,' vol. i.) make the elastic strength of iron and bronze in torsion to be from 0·625 to 0·735 of the strength in tension: for copper the ratio is about 0·545. The ratio of the ultimate strengths is a little higher. The ultimate strength in torsion should be determined by the use of the formula $T=\frac{2}{3}\pi q r^3$, which considers the whole of the material across a normal section to be in the same state of stress, but as the employment of this formula is not universal, the ratio of the ultimate stresses is open to suspicion.

12. *Previous experiments upon the Yield-point under Combined Stress.*—Beyond the numerous experiments upon torsion, the only experiments upon the yield-point which I have been able to find are those made upon pianoforte-wire by Mr. McFarlane for Lord Kelvin's article upon Elasticity in the *Encyclopædia Britannica.* These showed that a simultaneous tension lowered the yield-point in torsion, but numerical data are not given. Lord Kelvin concludes that as a tension lowers the torsional yield-point, a compression

would raise it; but his argument does not appear to be rigorous, and I venture to think that either tension or compression would lower it.

13. *Experiments upon Ultimate Strength under Combined Stress.*—Of experiments upon the ultimate strength under combined stress, there are the well-known experiments of Tresca, which show that a ductile material eventually behaves like a very viscous fluid, and a few experiments performed by Messrs. W. Voigt and L. Januszkiewiez on wax rods subjected to tension only, and to tension and external fluid pressure (compressed air) combined. In the latter case it was found that at rupture the shearing-stress in the material was the same in the two cases, thus agreeing with Tresca's experiments upon metals.

14. *Theories of Elastic Strength under Combined Stress: the Maximum Stress Theory.*—As examples of combined stress continually arise in practice, some working theory as to the criterion of strength, preferably elastic strength, must be assumed and adopted. Two theories hold the field to-day. The first is the assumption, it can hardly be called by any more ambitious name, that the material yields when one of the principal stresses reaches a certain amount, which must, by taking a special case, be the stress determined by a simple tension experiment. This was the theory adopted, in the absence of experimental data, by Rankine, and it is the one used by English and American engineers.

As all experiments upon torsion give results at wide variance with this theory, it can hardly be considered to be correct; and if it is used, a different working stress should be adopted in cases of torsion or systems of stress approximating thereto.

15. *The Maximum Strain Theory.*—The second theory is that the material yields when the greatest strain reaches a certain amount, which must, taking a special case, be the yield-point strain in simple tension. This theory was first advocated by St. Venant as fitting in with that molecular theory which leads to the uniconstant theory of elasticity. Upon this theory the value of Poisson's ratio, or the ratio of lateral contraction to axial extension of a specimen under simple tension, is 0·25; upholders of the theory maintaining that variations from this value which experiment exhibits are due

to imperfections of the material. The greatest-strain theory is that adopted upon the Continent, and is strongly upheld by many elasticians.

16. *Theorem upon the Limiting Values of* σ.—In the case of a cube of elastic material, whose elastic constants are E and σ (E being Young's modulus, or the ratio of stress to strain in a simple tension test), subjected to a uniform fluid pressure p, the linear contraction is $\frac{p}{E}(1-2\sigma)$. If the constitution of the material is to be stable, this must be a positive quantity, and hence the maximum value of σ is 0·5. This also shows that an isotropic stable material cannot decrease in volume under a simple tension (else it would decrease volumetrically under three orthogonal tensions).

It is hardly conceivable that σ should be negative, but it cannot be less than -1; otherwise the material would be unstable under torsion as the energy of a simple shear, $\frac{p^2}{E}(1+\sigma)$, would be negative should $1+\sigma$ be negative.

The values of σ met with in the course of experiments undertaken will be found in Table V. They are not determined by a method possessing much accuracy, being found from the values of E and C; they are, however, sufficiently accurate for the purpose in view.

17. *The Maximum Strain Theory not disproved by published experiments.*—Upon the maximum strain theory of strength the yield-point stress under torsion to that under tension should be 0·80 for cases in which $\sigma=0·25$. The least value of this ratio will occur when σ is a maximum, *i.e.* when $\sigma=0·5$, the value then being 0·66. As the experimental results quoted above place this ratio, for steel, between 0·625 and 0·735, it will be seen that, taking into consideration the effect of flaws upon a torsion test and the difficulty of locating the yield-point, the experimental results cannot be held to disprove the theory, although they militate against it.

In discussing the phenomena of torsion, Tresca separates the state of the material into three stages: the elastic state, the plastic stage, and an intermediate condition. These correspond to the portions OA, BC, and AB respectively in a stress-strain curve such as fig. 1. St. Venant, followed by many elasticians, does not recognize the intermediate stage, and considers that Hooke's law holds up to the point at which plasticity begins; he adopts Tresca's results that in the plastic stage the shearing-force is constant, and upholds a specific maximum strain as the condition of limiting elasticity.

I fail to understand how a material could have one condition for the commencement of plasticity and an entirely different one for its existence; perhaps users of these conditions tacitly admit the existence of the intermediate stage, but neglect it for the simplification of calculation and because the physical difference between the elastic and plastic states is so great; or perchance they do not admit the rigour of the deduction of the plastic law from Tresca's experiments. [St. Venant's proof (*Comptes Rendus*, lxx., and Todh. & Pearson's 'History of Elasticity,' vol. ii. § 236) that in the plastic stage the resistances to slide (shearing-strain) and elongation have the same value, consists in equating the work done in similar changes under a simple shear q and a combined stress $+p$ and $-p$, and hence showing that $q=p$. This is true in the elastic as well as in the plastic stage; but the combined stress $+p$ and $-p$ is merely another view of the shear, and constitutes a very different condition to a simple tensional stress, so that St. Venant's final step seems illogical.]

18. *The Maximum Shearing-Stress criterion of Elastic Strength.*—A third theory of elastic strength, mentioned by Cotterill in his 'Applied Mechanics,' is that the condition of yielding is the existence of a shearing-stress of a specific amount. Having regard to the behaviour of the material when in the plastic stage, the assumption of continuity would lead to this theory, but although the shearing-stress law of the plastic stage has been generally recognized, no formulas for elastic strength in particular cases have been based upon a similar law for the yield-point. The knowledge of Tresca's results and the observation of the phenomena presented by cold bending, tension and compression tests, punching, and the general manipulation of metal, must have urged many towards the conclusion that this is the true criterion of elastic strength in a ductile material.

19. *Further reasons for adopting Thin Tubes as specimens.*—It has been stated above, that tubular specimens were used in

this series of experiments. In addition to the reason there advanced, I was influenced by the advantage which tests made by subjecting the tubes to internal fluid-pressure would have in confirming, or not, the various theories. In such tests it is evidently an advantage to have the thickness of the tube small compared with the radius, as the stress will be more uniform, and the yield-point in consequence more sharply defined.

20. *Range of Stress covered by different types of experiment.*—If a specimen of circular section be submitted to torsion and tension combined in various ratios, the stresses at the exterior may be made to have all combinations between the pairs $-p$, $+p$, and 0, $+p$ [throughout I have considered tensions and elongations as positive, owing to their more frequent occurrence]; and if compression were substituted for tension the range between $-p$, $+p$, and $-p$, 0 would be included. Nothing beyond these, *i.e.* no like principal stresses can be produced by this method; these, however, can be readily impressed on the material of a hollow cylinder by the use of fluid pressure. By the combination of tension with internal pressure we can extend the range from 0, $+p$, to $+p$, $+p$; and by combining external pressure and axial force the range from $-p$, 0 to $-p$, $-p$ could be covered, but owing to the probable instability of a tube of suitable dimensions under these conditions, experiments upon this part of the range were deferred.

21. *Method of checking the Isotropism of the Material as regards Yield-point Stresses.*—This, however, is not the only advantage of the internal pressure and tension tests, for by their use we can check the isotropism of the material within the range $+\frac{1}{2}p$, p, by having the greater of the stresses first parallel to the axis and then circumferential: to do this within the range 0, $+\frac{1}{2}p$ it would be necessary to use a compressive load and internal pressure, as the longitudinal stress due to the internal pressure must be added to the longitudinal stress due to the externally applied load.

In addition, tests under the combination of internal pressure and torsion permit the principal axes of the stress to be inclined at varying angles to the generating lines of the specimen, and also, if a practical amount of isotropism has already been demonstrated by the internal pressure and tension tests, afford a check upon the general accuracy of the work by comparing the results of these tests with the results of experiments involving similar stresses differently applied.

Torsion tests on thin tubes, it may be noticed, cause a tendency in the wall to buckle, while the internal-pressure and tension tests do not. No buckling occurred in the experiments.

Although combined stresses may be produced by simpler methods, such as the loading of a cranked shaft or of a helical spring, such methods, since a small portion only of the material is carried to the yield-point condition, are hardly likely to furnish decisive results. It is essential for definition, both because of the elastic-limit effect and because of the smallness of the elastic strain, that the whole of the material directly under observation should be similarly stressed. The simplest methods of attaining this appeared to me to be those indicated above, namely, the application of axial loads, torques and internal pressures, singly or in pairs, to thin-walled circular tubes. As the production of thin-walled specimens otherwise than by drawing would be difficult, I determined to use seamless drawn tubing as specimens, and to remove the state of set left by the operation of drawing by annealing.

22. *Objections to Tubes on account of want of Isotropy.*—It has frequently been urged that no such material as wires, tubing, or sheet-metal can be regarded as isotropic; but I think such criticism may fairly be met by the consideration that in the production of ductile materials, operations producing sets and internal stresses, afterwards removed by annealing, are invariable and essential to the manufacture of a uniform material, and that annealing seems usually to remove this state of set. In the results of the tests shown, it will appear, at any rate so far as the occurrence of the yield-point was concerned, that the materials were practically isotropic.

In the case of experiments upon wires, which after annealing show a marked want of isotropy, it is probably due to overdrawing in the manufacture of the wire, which produces a series of conical defects along the wire, the effect of which evidently could not be removed by annealing. Unless the wire is wanted particularly hard for some special purpose, this defect is not likely to occur.

23. *Objection to Tubes on account of large effect of defects.*—Another objection, which can well be raised to the use of such thin-walled tubes as those which I experimented upon, is the large effect which would be produced by variations and defects in the specimen, especially in the torsion experiments. The tubes were all carefully examined before use, and none showing visible defects were employed; the greatest variation in external diameter was about 0·005 inch in 1·25 inch. This examination was intended, however, merely to avoid the waste of time which the testing of an obviously poor specimen would involve.

If any flaw existed in the material, or if the surfaces were not close approximations to concentric circular cylinders, the values of the elastic constants would be considerably changed, and always to a lower value; the density of the material would be low; and the stress-strain curve would soon cease to be straight.

Now in all the tests measurements of the distortions produced, as well as of the forces applied, were taken. The moduli of rigidity and extension calculated from these were never found to be widely different from their customary value, and especially they are never low in value. (See Table I.) Also the densities found were high. Furthermore, the stress-strain curves to within a point not far below the yield-point were always found to be straight.

24. *The System of Tests.*—The method of experimenting employed was, then, to subject the tubes to torque, to torque and tension combined, to tension only, to tension and internal pressure combined, to torsion and internal pressure combined, and to internal pressure only; and to take measurements of the axial elongation, of the twist when torque was employed, and in some cases of the circumferential strain. The range of the two principal stresses thus covered was from $-p$, $+p$ to $+p$, $+p$, the third principal stress being small, or zero.

25. *The Specimens and Holders.*—The specimens upon which the tests were made were formed of tubes (steel, copper, and brass) soldered on to holders, which served conveniently to apply the tension loads and the torques, and to introduce fluid

under pressure to the interior of the tube. A convenient size of tube appeared to be 1¼ in. diameter, with the walls from 0·025 in. to 0·036 in. in thickness. All measurements of extension and twist were made upon the same length of 8 in., but in order to provide room for the diametral extensometer which was sometimes used, and to avoid the disturbing effects of the holders upon the distribution of stress and strain, the length of tube free from the holders was a foot. A holder is shown in fig. 2. A is a screw connecting the holder to the jaw of the testing machine, it is adjusted so that the forces applying the torque have no vertical component—the specimen being vertical. B is a cross-bar serving to apply or to resist the torque. C is a passage-way for the oil used to apply the internal pressure. In the upper holder, which was the nearer to the weighing part of the testing machine, the exit was closed by a screwed cap ; sometimes a piece of rubber tubing, doubled over itself to form a packing, was pushed in ahead of the closing plug, and proved to be a very efficient means of preventing leakage. The exit was not closed until fluid appeared at it, in the expectation that should a tube prove unsound, or the pressure get beyond control, no damage would then be done to the strain-measuring apparatus. The lower holder was identical with the upper one, except that, in the place of the plug, a pipe was brazed into it, there being a coupling at the further end of the pipe for connexion with the pressure system.

26. *The Tension Loads.*—The tension loads were applied to the specimen by means of a Ten-ton Wickstead machine of the screw type. The shackles of the machine were fitted with the ball-thrust, or perhaps pull, bearings shown in fig. 2. The "male cone" surfaces C were made spherical in order that the specimen could line itself up to some extent and cause the axes of pull and of the specimen to coincide, and yet allow the specimen freedom to rotate. This action was assisted by gently tapping the specimen at low loads. The method of holding the specimen was by means of split collars D, the screw A of the tube-holder being thrust through the spherical cone of the ball-bearing so far as to allow the collars to be placed round it and inserted into the spherical cone. This proved a rapid and easy method of firmly securing

the specimens. I possessed no conveniences for calibrating the testing machine by the direct application of a large dead load, but the travelling poise (500 lbs.) was removed and found to be correct, and the distance between the knife-edges was measured, with the same result. In a few of the tests there was evidence that the axes of the specimen and of the pull did not exactly coincide, causing a small bending moment on the specimen. This tends to produce an effect similar to that of the elastic limit.

27. *The Application of the Torque.*—In order to apply torque to the specimen, it was placed in the testing machine and a small load (250 lbs.) placed upon it, to line it up and steady it. The cross-bars were then placed in the holders and nipped in position by the set screws E. Steel points F were then placed in the upper cross-bar, and a pair of screws in a bracket, bolted to the casting of the testing machine, were adjusted to just touch the lower cross-bar. Finally, equal and opposite forces were applied to the steel points by means of bent pieces of iron, as shown in the left-hand top corner of fig. 2, attached to belts. These belts were belt laces, which being thin, flexible, and sufficiently strong, appeared to be the best means of transmitting round pulleys such forces as were required. The belts led off horizontally from the ends of the cross-bar, which was adjusted vertically by the screw A of the tube-holders, to pulleys, from which they went vertically downwards to knife-edges fixed in the ends of a horizontal cross lever, from a knife-edge at the centre of which hung the carrier for the weights which produced the torque. The effect of the cross lever and weight-carrier was neutralized by balance-weights hung over the pulleys. These pulleys were made by filling the rims of bicycle wheels with plaster-of-paris, and, before the plaster had set hard, rotating the wheel in contact with a former, thus producing a suitable groove true with the axis of rotation. The torque thus applied to the specimen was practically pure, and produced no bending moment on the specimen. It was resisted by the forces produced by the set screws on the lower cross-bar, there being thus little or no sideways force at the lower grip.

28. *The Friction of the Torsion Rigging.*—A fourth pulley

was used in testing the friction of the torsion apparatus. The greater part of this friction, when any considerable load was on the specimen, occurred in the ball-bearings in the shackles. To ascertain the friction two equal and opposite torques were applied to the top cross-bar by means of belts leading over each of four pulleys and terminating in a weight-carrier. The lower cross-bar was removed. The desired tension load P was then placed upon the specimen, and approximately equal additional weights placed upon a diagonally opposite pair of weight-carriers until they descended. The equal additional weights were placed upon the other pair of weight-carriers until they in turn descended. The latter pair of additional weights (shot) were then placed together and weighed. One quarter of this amount for one of the weights on the carriers represents the equivalent of the friction of the system under the load P. Now in this test four pulleys and the two shackle bearings rotate, while in the actual tests three pulleys and one shackle-bearing are rotated, thus the previous result should be halved for application to the tests. The two weights on the carriers are, however, combined into one hung at the centre of the cross-lever, so that one quarter of the weighed amount should be taken for the weight (W) at the centre of the cross-lever. The results of these friction tests are given in Table I.; the friction given is in all cases too high, as, the masses moved being large, a small moving force produced a small acceleration which required considerable time to make its effect manifest. The corrections required for W are so small that they have been neglected in the calculations of the stresses.

Table I.

Friction of Torsion Apparatus.

It was found that the friction of the pulleys was so small as to be negligible in comparison with the friction of the pull-bearings, the value of W making little difference.

Mean values of δW from several experiments are given :—

P	1000	2000	3000	4000
δW	0·319	0·576	0·909	1·058

Hence $\delta W = 0{\cdot}285$ lb. per 1000 lb. value of P.

And $\delta W = 0{\cdot}075$ lb. in all cases for the wheels.

Hence Friction only amounts to 1½ lb. for a load of 5000 lbs.

29. *The Application of the Internal Pressure.*—When tests involving the application of internal pressure were to be made, after a small tensional load had been placed on the specimen so as to line it up, the lower end was clamped firmly by the other screws, opposite to the first set, in the bracket (fig. 4, A). The tube brazed into the lower holder was then clamped at two points to the lower cross-bar, and finally the tube was coupled to the pressure system. The clamps were intended to prevent the production of a bending-moment on the specimen ; but in spite of these precautions, and although the pipe conveying the pressure was long and thin, evidence of a bending-moment (small, however) was evinced in some of the tests.

This could have been avoided in the tension-internal pressure tests by generating the fluid pressure in a reservoir attached to the specimen, the plunger being connected to the jaw of the testing machine, thus transmitting the pull and producing the fluid pressure at the same time. This method, however, only permits of a certain ratio of fluid pressure to tensional load for a given plunger, is inapplicable to torsion-internal pressure tests, and is subject to other objections. Accordingly the former method, despite the risk incurred of an undesired bending-moment, was adopted.

Up to 1000 lbs. per sq. in. the pressure was taken from the system which worked the hydraulic straining-gear of an Emery-Festing machine ; beyond that pressure a small intensifier was employed to further increase the pressure.

30. *Measurement of the Fluid Pressure.*—To measure the pressure I invented a special form of gauge, but although this proved useful for calibrating purposes, it was replaced in the tests by a large commercial gauge, which could be read by means of a telescope from the controlling-valve of the Emery pressure-system, which valve was at a considerable distance from the Wickstead machine. This commercial gauge was calibrated by comparison with the volume of air compressed into a uniform tube by the pressure and by comparison with the special gauge, the constant of which was determined at a low load by means of a Crosby gauge-tester. The air-gauge consisted of a glass tube of about 1 mm. diameter of bore and 1 metre long, sealed hermetically

into a glass bulb holding about 20 c.c.; below this a tube projected downwards, and was then bent upwards for convenience in handling. The capillary tube was selected as having the most uniform bore of a large number of such tubes, and was so even as to render correction for conicallity unnecessary. The bulb of the glass apparatus was contained in a iron cylinder partially filled with mercury, to the top of which the oil of the pressure-system had access. The iron cylinder was closed with a screw plug, through which the capillary tube projected; the packing used was of the U-type. The comparison of the volume of air under pressure with the reading of the commercial gauge was conducted so slowly that the changes of volume were practically isothermal. The volume of the tube and of the bulb, and the quantity of air contained, had been carefully measured, but a large quantity of air was syphoned out by the action of the mercury; and in preference to running the risk of an unnoticeable quantity being syphoned out, the pressure at 300 lbs. per square inch was determined by the use of a Crosby gauge-tester, so that this is the ultimate basis of the measurement of the fluid pressure.

31. *A new type of Pressure-gauge.*—The special gauge (see fig. 3) consisted of a steel tube of oval section, twisted along its axis, so that the tube had a straight axis, but the extremities of the major axes of the sections perpendicular to the tube-axis lie on a pair of helices the angle of which is about 45° to 60°. One end of the tube is coupled to the pressure-system, and the free end is sealed up and a pointer or mirror, preferably the latter, mounted upon it. On the application of internal pressure the tube untwists, and the amount of angular movement is determined by the use of a telescope and scale, or in any other manner. As the strain at any part is small, it is proportional to the pressure; but the integral twist of the mirror or pointer may be made of any magnitude we please, without exceeding the elastic limit of the metal, by simply increasing the length of the gauge-tube. As, by using a tube of suitable thickness, it is easy to keep the stresses in the steel, produced by fluid pressures up to several thousand pounds per square inch, below the yield-point, and since there is no mechanism nor friction, the gauge

is at once simple and accurate. By comparing the readings of two gauges, one having thicker walls than the other, the fluid pressure corresponding to the yield-point of the lighter gauge can easily be found, as it occurs when the readings cease to be proportional. The constant of the heavy pressure-gauge may be found by comparing it with the lower gauges. Having first ascertained the permissible working pressures, a thin-walled gauge may be compared with a mercury column, and its constant thus found; this gauge may then be compared with a heavier gauge, and since the constant of the first gauge cannot alter, that of the second may be found. Thus the constants of all the gauges can be found. The axis of such a gauge-tube can evidently be coiled (as a line) and produce other desirable movements.

The gauge used in the calibration of the commercial gauge was made of tubing originally $\frac{1}{4}$ inch in diameter; it was about 8 inches long, and from my knowledge of the yield-points of thinner-walled gauges I think that its yield-point would be reached under a fluid pressure of from 4000 to 5000 lbs. per square inch.

In Table II. will be found the comparison of the commercial gauge by the two methods. They give practically the same result.

TABLE II.

Gauge Calibration: Comparison of Pressures in lbs. per sq. in., as determined by the different Gauges.

Commercial.	Air.	Special.	Commercial.	Special.
200	...	196	1100	1030
300	290	290	1200	1120
400	380	...	1300	1220
500	475	475	1400	1320
600	570	565	1500	1420
700	665	662	1600	1520
800	750	740	1700	1610
900	850	851	1800	1705
1000	...	935	1900	1795
			2000	1895

32. *Measurement of the Distortions.*—In order to determine the strains and to locate the points in the various stress-strain curves, I used instruments which I had devised with a

view to these tests. They were a combined axial extensometer and twist-meter, and a diametral extensometer used to determine the circumferential strain.

As it seems to be essential that any extensometer to be used on a part of the stress-strain curve likely to involve a time-effect should be single-reading, and should not be required to be manipulated in any way to obtain a reading, optical methods were used throughout.

33. *A New Extensometer.*—It will be convenient to describe the axial portion of the apparatus first. It consists of a lever-system and a mirror; the twist of the latter, produced by an extension of the specimen in a manner similar to the Unwin extensometer, being read by a telescope and scale. The various parts are shown in fig. 4, which is a side-elevation of the whole instrument in position on a specimen, the "adjuster" being shown on the left-hand side. The piece marked 1 is called the adjuster, and serves to adjust the grips 2 and 3 correctly on the specimen, so that they are at the correct distance apart, and so that certain points in their configuration lie on the axis of the specimen. In fig. 5 is shown a view from below the grip 2 in fig. 4, and in the broken lines is shown a view of the end of the adjuster. This adjuster consists of surfaces A_1, A_2, A_3, A_4, of which A_1 and A_3 are parts of one plane, and A_2, A_4 are parts of another intersecting it. CD and EF are portions of kinematic slides for the grips 2 and 3, the other elements of the slides being formed by the spheres c_1, c_2, d on the grip 2, and e_1, e_2, f on the grip 3, which is shown in fig. 7. These are so arranged that the axis of the screws G, H, and the line st referred to later, will bisect the angle between the planes A_1, A_3 and A_2, A_4, and be perpendicular to their intersection. It is evident that by this arrangement the lines GH and st will pass through the axis of the specimen (whatever be its size), which is necessary for the determination of the mean extension should the specimen stretch unequally, owing to bending-moment or other cause. At B is shown a hole, which is at the back of the adjuster, through which a rubber band is passed to support the adjuster on the specimen while the grips are being fastened. The spheres c_1, c_2, d of the grip 2 are placed in the V-groove C and on the plane D,

Fig. 4. Extensometer, side elevation.
5. " details.
6. " "
7. " "
8. " "
9. " "

Fig. 10. Apparatus for measuring Twist.
11. " " "
12. " " "

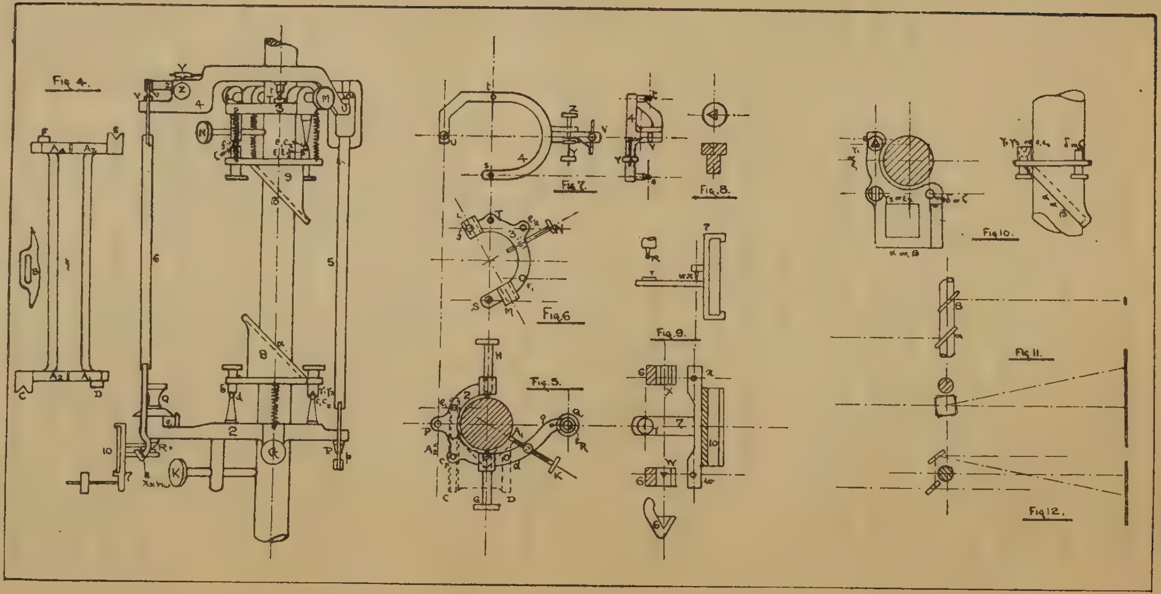


TABLE III.

Experiments to test Extensometer.

Swedish Iron specimen, previously tested; mean diam. 0·628 in.; length 8·00 in
Extensometer-reading multiplied by 0·000001265 = strain.

Load in lbs.	Extensometer-Readings.					
	In-creasing.	De-creasing.	In-creasing.	De-creasing.	In-creasing.	De-creasing.
500	043	045	...	265	...	264
1000	086	090	086	311	307	
1500	129	133	...	356	350	354
2000	172	176	171·5	399	393	
2500	215	220	...	443	437	441
3000	258	263	258	486	480	
3500	301	305	...	530	523	528
4000	344	347	344	573	566	
4500	387	390	...	616	610	613
5000	430	434	430	659	654	
5500	472	475	...	701	696	698
6000	515	516	515	743	738	
6500	558	...	...	785	781	
7000	...	...	599	826		
,,	...	...	607			
710	...	...	617 &c.			

	In-creasing.	De-creasing.	In-creasing.	De-creasing.
1800	...	–016		
1900	...	–007·5	–008	
2000	000	000·5	000	
2100	008	009		
2200	016			
3500	...	–043		
3750	...	–021	–022	
4000	...	000	–001	–002
4250	...	...	+021	020
4500	...	...	041	

and the grip slid along into position and the screws G, H nipped into the specimen; the screw R is then adjusted to touch the specimen. The other grip is adjusted in the same manner, and the adjuster is then withdrawn. It will be seen that the grips form one piece with the specimen, and during a test the screw-points are not employed as bearings, the friction at which would be an unknown variable quantity.

The bottom grip 2 is fitted with a trihedral hole (see fig. 9) at P, in which lies a steel ball p fastened to the length-bar 5 (fig. 5), the pair forming a universal joint. Similar universal joints are to be seen at Uu, Ss, Vv, Rr, and Ww. The length-bar connects the grip 2 with a bent lever 4 (fig. 8), which rests on the top grip 3; the length-bar being connected to the lever by the universal joint Uu, and the lever being kinematically hinged to the top grip by the universal joint Ss and a sphere t working in a V-groove T. The axis of the screws L, M intersects and bisects the line st, and the grip 2 is so adjusted that the point of intersection is on the axis of the specimen. To the other end of the lever is connected, by the universal joint Vv, the mirror-bar 6 (figs. 4 & 9), to which the mirror-frame, 7, is hinged kinematically by the universal joint Ww and the V-groove and sphere Xx. The mirror-frame 7 (figs. 4 & 7) is finally connected to the lower grip, 2, by the universal joint Rr, the sphere R being carried on the end of the calibrating-screw Q. In addition to the restraints mentioned, the mirror-bar has a wing, z, which is in contact with the (blunt) end of a screw Z, being kept in contact by the small weighted lever Y. Any extension of the specimen will result in an angular movement of the lever 4, thus raising the axis of the hinge WX, and causing the mirror to rotate about this axis. It will be noticed that the forces along all the members of the instrument are practically unaffected by the movements of the parts, being controlled by the position of the adjustable weight shown on the mirror-frame. The mirror is readily adjusted, so that the reflexion of the scale appears in the field of view of the telescope by means of the screw Z, which turns the mirror about a vertical axis, while the scale-reading can be adjusted to zero by means of the screw Q. This screw also serves, in case it should be desired to push the investigations beyond the yield-point, to readjust the reading on to the scale as often as desired, and also to ascertain directly the value of a scale-division in terms of the axial strain. To do this the change of scale-reading caused by one or more turns of the screw, the head of which is graduated and the pitch of which is known; then, by taking account of the multiplication by the levers and of the length of the specimen, the axial strain per scale-division is easily found. The screw Q was compared directly with a Brown and Sharpe micrometer, and the two were found to agree to the $\frac{1}{10,000}$ inch in eight turns or 0·2 inch. A consideration of the behaviour of the instrument under the supposition that the specimen bends or twists will show that these do not affect the reading, which will always represent the mean axial elongation. One kinematic restraint, it will be noticed, is wanting: this, however, would be supplied by a wing attached to the length-bar and arrangements similar to YZ, but would have no effect on the working of the instrument; it is therefore omitted. Figs. 5, 6, 7, 8, and 9 represent parts of the extensometer: fig. 6 being the top grip, 7 the lever, 8 a trihedral hole, and 9 a side-view and sectional plan of the mirror and its supports, on a rather larger scale than the other parts.

The instrument proved sensitive and trustworthy; the tests of it for sensitiveness made on the Norwegian iron specimen previously referred to are given in Table IV. The scale was placed at such a distance that the extension in 8 inches corresponding to one scale-division was about the one hundred thousandth of an inch; the nearest scale-division is recorded, except when the cross-hair of the telescope was apparently midway between two divisions.

34. *Errors of Extensometer.*—In a figure formed by plotting out Table IV. it can be noticed that the hysteresis-loop, due to the yield-point having been reached previously, is well marked, and its width is considerably greater than the instrumental error; the errors, which are quite insignificant, are about the value of one scale-division, and include any error due to the want of sensibility of the testing-machine.

35. *A New Twist-measuring Apparatus.*—The apparatus for measuring the twist consisted merely of a pair of mirrors mounted on the grips 2 and 3, a scale placed horizontally being read by light reflected at each of the mirrors. Two arrangements occurred to me: one in which the mirrors had their normals perpendicular to the axis of the specimen (see fig. 12), and one in which they were inclined at 45° or so (see figs. 10 & 11). In these figures the course of the ray of light is indicated roughly by the broken line, the scale

being shown at the right-hand side, and the telescope or source of light being upon the left. The amount of twist of the specimen is determined by observing the change of reading of the scale by means of a telescope, the scale being observed by reflexion at both of the mirrors.

The second was the method selected, it being easily applicable to specimens of varying lengths.

The mirrors are mounted upon frames resting upon the spheres c_1, c_2, d ; e_1, e_2, f of the grips, which are left vacant by the withdrawal of the adjuster. The two frames are exactly similar. The angle c_1, c_2, d is a right angle ; the contact of the frame with c_1, b is made by means of a trihedral hole mounted on a screw, with c_2 by means of a fixed V-groove, and with d by means of a plane at the end of a screw. The normals to the mirrors can be adjusted within certain limits by the use of these screws. The various surfaces are kept in contact by the use of the springs shown in fig. 4.

Had the other method been adopted, one or both mirrors would have had to have been mounted upon sliding bars so that they could have been adjusted opposite to one another, when the grips (for torsion purposes) were placed at various distances apart. No special adjustment, however, would have been required to secure accuracy.

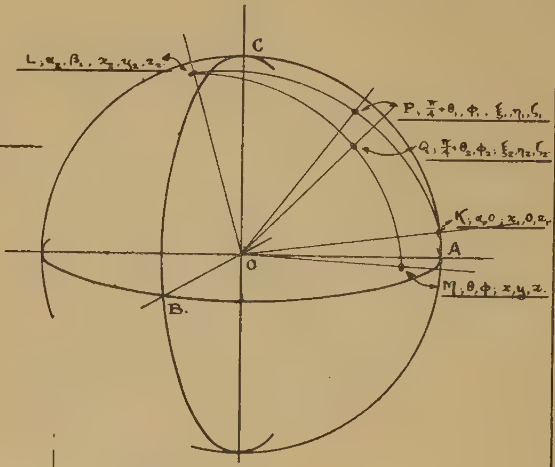
If, in the inclined mirror case, we consider the lower grip stationary and the top mirror alone to twist, it is very evident that the twist of the upper mirror is the same as the angle through which the reflexion of the optical axis of the reading-telescope is turned, and is therefore, to the second order of small quantities, equal to the change of scale-reading divided by the distance from the telescope to the scale. The lower grip, however, must be allowed to twist in order that the stress in the specimen between the grips may be of the normal type, uninfluenced by the proximity of the holders ; in the following investigation it will be shown that, when a certain adjustment is made, the scale-reading divided by the distance from the specimen to the scale is equal to the twist of the specimen between the grips, at any rate as closely as the tangent of the angle is equal to the angle.

36. *Proof that the Torsion-Mirrors measure the Twist.*—The light from the scale first strikes the upper mirror, and is thence reflected on to the lower mirror, whereby it is reflected to the telescope. In order, however, to ascertain the effect of a simultaneous twist of the two grips, we shall take the line in the reverse direction, and consider the optical axis of the telescope and the direction of its reflexions at each of the mirrors. The distance between the mirrors will be neglected, as it should be small compared with the distance from the specimen to the scale, or else a lens should be placed between the top mirror and the scale to render the light proceeding from the latter parallel. In the apparatus as rigged for the tests, the distance between the mirrors was 2 or 3 inches, and the distance to the scale over 200, so that this condition was satisfied.

In fig. 13, OC is the axis of the specimen, OA is perpendicular to OC and in the plane of the optical axis of the telescope, OB is perpendicular to OA and OC. The line OK, coordinates $\frac{\pi}{2}-\alpha_1$, 0 or x_1, 0, z_1, is the optical axis of the telescope, and cuts a sphere of unit radius whose centre is O in the point K. The normal to the mirror nearest the telescope is represented by OP, coordinates $\frac{\pi}{4}+\theta_1$, ϕ_1; or ξ_1, η_1, ζ_1. The reflexion of OK in the mirror is OL, coordinates α_2, β_2, or x_2, y_2, z_2, so that OL represents the path of the ray between the mirrors. The normal to the upper mirror is represented by OQ, coordinates $\frac{\pi}{4}+\theta_2$, ϕ_2, or ξ_2, η_2, ζ_2; this line is shown drawn in the same octant as the other lines for the sake of clearness, though it should actually be reversed; but a little consideration will show that, by considering the light to come in the direction LO, it will, after reflexion in the second mirror, proceed in the direction OM, coordinates θ, ϕ or x, y, z; while the actual ray of light will merely be in the direction KO, instead of OK. The quantities α; the error of setting the telescope in altitude; θ_1, θ_2 the errors of setting the mirrors; and ϕ_1 and ϕ_2, the azimuthal movements of the mirrors, are supposed small, ϕ_2 being considerably larger than any of the others.

Fig. 13. Diagram for Twist-meter.
14. Diametral Extensometer.
20. Three-dimensional view of tests.

Fig 13.


$L;\ \alpha_2, \beta_1, x_2, y_2, z_2$
C
$P,\ \frac{\pi}{4}+\theta_1, \phi_1, \xi_1, \eta_1, \zeta_1$
$Q;\ \frac{\pi}{4}+\theta_2, \phi_2;\ \xi_2, \eta_2, \zeta_2$
$K;\ \alpha, 0;\ x_1, 0, z_1$
A
O
$M;\ \theta, \phi;\ x, y, z.$
B.

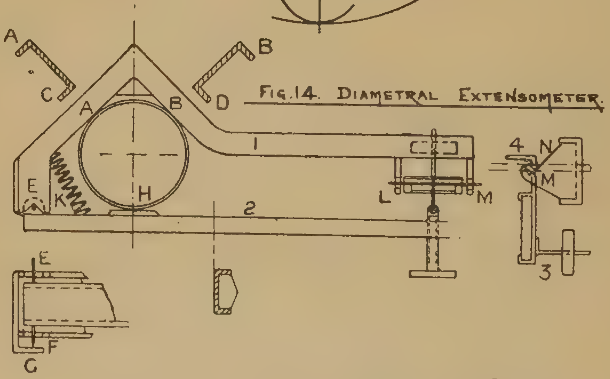
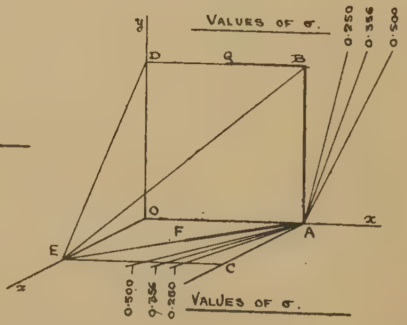


Fig.14. Diametral Extensometer.

Fig. 20.



Then $x_1 = 1$ nearly, z_1 is small;
$z_2 = 1$ nearly, x_2 and y_2 are small;
$x = 1$ nearly, y and z are small.

We have to find θ and ϕ or x, y, z.

Also the coordinates of

K are $x_1\ y_1\ z$ or $1-\frac{\alpha_1^2}{2}$; 0; α_1.

P are $\xi_1\ \eta_1\ \zeta_1$,

or

$$\sin\overline{\frac{\pi}{4}+\theta_1}\cos\phi_1\,;\quad \sin\overline{\frac{\pi}{4}+\theta_1}\sin\phi_1\,;\quad \cos\overline{\frac{\pi}{4}+\theta_1}\,;$$

or

$$\frac{1}{\sqrt{2}}\left\{1+\theta_1-\frac{\theta_1^2}{2}-\frac{\phi_1^2}{2}\right\};\quad \frac{1}{\sqrt{2}}(1+\theta_1)\phi_1\,;\quad \frac{1}{\sqrt{2}}\left\{1-\theta_1-\frac{\theta_1^2}{2}\right\}.$$

Q are $\xi_2\ \eta_2\ \zeta_2$,

or

$$\sin\overline{\frac{\pi}{4}+\theta_2}\cos\phi_2\,;\quad \sin\overline{\frac{\pi}{4}+\theta_2}\sin\phi_2\,;\quad \cos\overline{\frac{\pi}{4}+\theta_2}\,;$$

or

$$\frac{1}{\sqrt{2}}\left\{1+\theta_2-\frac{\theta_2^2}{2}-\frac{\phi_2^2}{2}\right\};\quad \frac{1}{\sqrt{2}}\left(1+\theta_2-\frac{\theta_2^2}{2}\right)\phi_2\,;\quad \frac{1}{\sqrt{2}}\left(1-\theta_2-\frac{\theta_2^2}{2}\right).$$

To find L or $x_2\ y_2\ z_2$, we have:—

(1) Since $\angle\text{LOP} = \angle\text{KOP}$,

$$x_2\xi_1 + y_2\eta_1 + z_2\zeta_1 = \xi_1 x_1 + \eta_1 y_1 + \zeta_1 z_1 \quad . \quad . \quad . \quad . \quad (1)$$

And (2), since LOPK is a plane,

$$\begin{vmatrix} x_2 & y_2 & z_2 \\ \xi_1 & \eta_1 & \zeta_1 \\ x_1 & y_1 & z_1 \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$x_2^2 + y_2^2 + z_2^2 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence from (1)

$$x_2\left(1+\theta_1-\frac{\theta_1^2}{2}-\frac{\phi_1^2}{2}\right)+y_2(1+\theta_1)\phi_1+z_2\left(1-\theta_1-\frac{\theta_1^2}{2}\right)$$

$$=\left(1+\theta_1-\frac{\theta_1^2}{2}-\frac{\phi_1^2}{2}\right)\left(1-\frac{\alpha_1^2}{2}\right)+\left(1-\theta_1+\frac{\theta_1^2}{2}\right)\alpha_1, \quad . \quad (4)$$

or to the first order

$$x_2(1+\theta_1)+y_2\phi_1+z_2(1-\theta_1)=1+\theta_1+\alpha\,; \quad . \quad . \quad (4a)$$

$$\therefore \quad x_2+z_2=1 \text{ to first order.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From (2)

$$\begin{vmatrix} x_2 & y_2 & z_2 \\ 1+\theta_1-\dfrac{\theta_1^{\,2}}{2}-\dfrac{\phi_1^{\,2}}{2}, & (1+\theta_1)\phi_1, & 1-\theta_1-\dfrac{\theta_1^{\,2}}{2} \\ 1-\dfrac{\alpha_1^{\,2}}{2} & 0 & \alpha_1 \end{vmatrix}=0;$$

or

$$x_2\phi_1\alpha_1+y_2\left(1-\alpha_1-\theta_1-\alpha_1\theta_1-\frac{\theta_1^{\,2}}{2}-\frac{\alpha_1^{\,2}}{2}\right)-z_2(1+\theta_1)\phi_1=0;(6)$$

or to the first order,

$$y_2(1-\theta_1-\alpha_1)-z_2\phi_1=0\,; \quad . \quad . \quad . \quad . \quad (6a)$$

hence y_2 is a small quantity.

Substituting in (3),

$$x_2^{\,2}+z_2^{\,2}=1,$$

which combined with (5) gives us as values $x_2=0$ and $z_2=1$. (The values $x_2=1$ and $z_2=0$ correspond to K.)

Also it is evident that $1-z_2=\lambda$ is of the second order. [For

$$\begin{aligned} x_2^{\,2}+y_2^{\,2}+z_2^{\,2}&=x_2^{\,2}+y_2^{\,2}+(1-\lambda)^2 \\ &=1-2\lambda+(x_2^{\,2}+y_2^{\,2}+\lambda^2); \end{aligned}$$

$\therefore$ λ is of second order.]

$\therefore$ (4a) becomes $\quad x_2-\theta_1=\theta_1+\alpha_1,$

and (6a) becomes $\quad y_2-\phi_1=0;$

hence

$$\left.\begin{aligned} x_2&=2\theta_1+\alpha, \\ y_2&=\phi_1, \\ z_2&=1, \end{aligned}\right\} \text{ to first order.}$$

Let the terms of the second order in x_2, y_2, z_2 be λ, μ, ν

respectively; then from (4)

$$(2\theta_1+\alpha_1+\lambda)(1+\theta_1)+\phi_1{}^2+(1+\nu)\left(1-\theta_1-\frac{\theta_1{}^2}{2}\right)$$
$$=\left(1+\theta_1-\frac{\theta_1{}^2}{2}-\frac{\phi_1{}^2}{2}\right)\left(1-\frac{\alpha_1{}^2}{2}\right)+\left(1-\theta_1-\frac{\theta_1{}^2}{2}\right)\alpha.$$

Hence

$$\lambda+\nu=-2\theta_1{}^2-2\alpha_1\theta_1-\frac{\alpha_1{}^2}{2}-\frac{3}{2}\phi_1{}^2. \quad . \quad . \quad (7)$$

Substituting in (3),

$$4\theta_1{}^2+4\theta_1\alpha_1+\alpha_1{}^2+\phi_1{}^2+1+2\nu=1\,;$$
$$\therefore \quad \nu=-\left(2\theta_1{}^2+2\theta_1\alpha_1+\frac{\alpha_1{}^2}{2}+\frac{\phi_1{}^2}{2}\right);$$
$$\therefore \quad \lambda=-\phi_1{}^2\,;$$

and substituting in (2),

$$\begin{vmatrix} 2\theta_1+\alpha_1+\lambda, & \phi_1+\mu, & 1+\nu \\ 1+\theta_1-\frac{\theta_1{}^2}{2}-\frac{\phi_1{}^2}{2}, & \phi_1+\theta_1\phi_1, & 1-\theta_1-\frac{\theta_1{}^2}{2} \\ 1-\frac{\alpha_1{}^2}{2}, & 0, & \alpha_1 \end{vmatrix}=0.$$

From which we get

$$\mu=\phi_1(2\theta_1+\alpha_1).$$

So that to the second order of small quantities,

$$\left.\begin{aligned} x_2&=2\theta_1+\alpha-\phi_1{}^2, \\ y_2&=\phi_1+\phi_1(2\theta_1+\alpha_1), \\ z_2&=1-2\theta_1{}^2-2\theta_1\alpha_1-\frac{\alpha_1{}^2}{2}-\frac{\phi_1{}^2}{2}. \end{aligned}\right\}$$

We now proceed to find x, y, z from equations similar to (1), (2), and (3), namely,

$$x\xi_2+y\eta_2+z\zeta_2=x_2\xi_2+y_2\eta_2+z_2\zeta_2, \quad . \quad . \quad . \quad . \quad (8)$$

$$\begin{vmatrix} x & y & z \\ \xi_2 & \eta_2 & \zeta_2 \\ x_2 & y_2 & z_2 \end{vmatrix}=0, \quad . \quad . \quad . \quad . \quad (9)$$

and $$x^2+y^2+z^2=1.$$

Equation (8) becomes

$$x\left(1+\theta_2-\frac{\theta_2^2}{2}-\frac{\phi_2^2}{2}\right)+y(1+\theta_2)\phi_2+z\left(1-\theta_2-\frac{\theta_2^2}{2}\right)$$
$$=(2\theta_1+\alpha_1-\phi_1^2)(1+\theta_2)+\{\phi_1+\phi_1\overline{2\theta_1+\alpha_1}\}(1+\theta_2)\phi_2$$
$$+\left(1-2\theta_1^2-2\theta_1\alpha_1-\frac{\alpha_1^2}{2}-\frac{\phi_1^2}{2}\right)\left(1-\theta_2-\frac{\theta_2^2}{2}\right); \quad . \quad (10)$$

or to the first order,

$$x(1+\theta_2)+y\phi_2+z(1-\theta_2)=2\theta_1+\alpha_1+1-\theta_2. \quad . \quad (10\,a)$$
$$\therefore\ x+z=1.$$

Equation (9) becomes

$$\left|\begin{array}{ccc} x & y & z \\ 1+\theta_2-\frac{\theta_2^2}{2}-\frac{\phi_2^2}{2}, & \phi_2(1+\theta_2), & 1-\theta_2-\frac{\theta_2^2}{2} \\ 2\theta_1+\alpha_1, & \phi_1 & 1 \end{array}\right|=0;$$

hence

$$x\{\phi_2(1+\theta_2)-\phi_1(1-\theta_2)\}+y\left\{\overline{2\theta_1+\alpha_1}(1-\theta_2)-\left(1+\theta_2-\frac{\theta_2^2}{2}-\frac{\phi_2^2}{2}\right)\right\}$$
$$+z\{\phi_1(1+\theta_2)-\phi_2(2\theta_1+\alpha_1)\}=0; \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or to the first order,

$$x(\phi_2-\phi_1)+y(2\theta_1+\alpha-1-\theta_2)+z\,.\,\phi_1=0; \quad . \quad . \quad (11\,a)$$

therefore y is small,

and $\qquad x^2+z^2=1$ to the second order,

and $\qquad x\ +z\ =1$ to the first order.

$\therefore\ x=1$ and $z=0$.

[The solutions $x=0$, $z=1$ refer to the point L.]

$\therefore$ as before, $x=1$ to the second order.

From (10 a) $\qquad 1+\theta_2+z=2\theta_1+\alpha_1-\theta_2,$

$$\therefore\ z=2\theta_1-2\theta_2+\alpha;$$

and from (11 a) $\qquad \phi_2-\phi_1-y=0,$

$$\therefore\ y=\phi_2-\phi_1.$$

Hence
$$x=1+\rho,$$
$$y=\phi_2-\phi_1+\sigma,$$
$$z=2(\theta_1-\theta_2)+\alpha+\mathrm{T},$$

where ρ, σ, and T are quantities of the second order.

To find σ consider equation (11), it becomes

$$\begin{vmatrix} 1+\rho, & \phi_2-\phi_1+\sigma, & 2\theta_1-2\theta_2+\alpha+\mathrm{T} \\ 1+\theta_2-\frac{\theta_2^2}{2}-\frac{\phi_2^2}{2}, & \phi_2+\theta_2\phi_2, & 1-\theta_2-\frac{\theta_2^2}{2} \\ 2\theta_1+\alpha_1+\phi_1^2, & \phi_1+\overline{2\theta_2+\alpha}\,.\,\phi_1, & 1-2\theta_1^2-2\theta_1\alpha_1-\frac{\alpha_1^2}{2}-\frac{\phi_1^2}{2} \end{vmatrix}=0.$$

The terms of the second order are

$$\theta_2\phi_2-\overline{2\theta_1+\alpha}\phi_1+\theta_2\phi_1+\overline{\phi_2-\phi_1}(2\theta_1+\alpha_1-\theta_2)-\sigma$$
$$+(2\theta_1-2\theta_2+\alpha)\phi_1=0\,;$$
$$\therefore\ \sigma=(\phi_2-\phi_1)(2\theta_1+\alpha).$$

Hence we see that the scale-reading is $(\phi_2-\phi_1)(1+2\theta_1+\alpha)$, and that the horizontal cross-hair of the eyepiece will move across the image of the scale through an angle δz or $\delta(2\overline{\theta_1-\theta_2}+\alpha)$. This remains constant, so that the movement across the scale due to twist of the specimen is very small. Now in the use of this instrument ϕ_2 is of a larger order than any of the other quantities, but if the other quantities ϕ_1, θ_1, θ_2, and α are all zero, it is evident that ϕ and ϕ_2 are exactly equal.

Hence $$\phi=(\phi_2-\phi_1)(1+2\theta_1+\alpha)$$

to quantities of the orders

$$\phi_2^3,\ \phi_1^2,\ \theta_1^2,\ \theta_2^2,\ \alpha_1^2.$$

Now put $$\phi_2=\phi_1=0.$$

Then the ray lies in the plane COA, and

$$\begin{aligned} \mathrm{COZ}&=\mathrm{COP}-\mathrm{LOP}=\mathrm{COP}-\mathrm{KOP} \\ &=\mathrm{COP}-(\mathrm{AOP}-\mathrm{AOK}) \\ &=\frac{\pi}{4}+\theta_1-\left(\frac{\pi}{4}-\theta_1\right)+\alpha_1 \\ &=2\theta_1+\alpha_1. \end{aligned}$$

Hence if we make the reflexion of the optical axis in the first mirror parallel to the axis of the telescope, the value of ϕ becomes $\phi_2-\phi_1$, or the scale-reading divided by the distance to the scale is the twist between the mirrors to the orders of small quantities stated above. This adjustment is made by the use of the adjusting-screws of the lower mirror, the telescope being sighted so as to have the lower mirror at the centre of its field, and then the mirror adjusted so that a point similarly situated with respect to the specimen as the centre of the lower mirror appears at the centre of the field.

The adjustment was tested by turning the specimen as a whole through an angle of 0·1, when it was found that the scale-reading changed through an angle corresponding usually to about 0·001.

The greatest value of ϕ_2 was about 0·05, the cube of which is 0·000125; the corresponding value of ϕ_1 would be about one-eighth of ϕ_2 or 0·006, and $\phi_2{}^2$ would be 0 00004. The error of ϕ would hence be about 0·25 per cent., which is quite negligible.

It will be noticed that azimuthal errors in the settings of the mirrors are of no effect, being parts of ϕ_2 and ϕ_1, changes of which alone affect the value of ϕ.

37. *The Effect of Bending.*—Unfortunately, the effect of bending * was not investigated until the series of tests had been practically completed; otherwise the alternative arrangement of the twist-mirrors, which is free from such defects, would probably have been preferred although not readily applicable to specimens of different lengths.

Bending in a plane through the telescope and specimen has the effect of causing the image of the scale to move vertically across the field of the telescope, but it does not affect the reading.

Bending in a plane at right angles to this, however, has an effect upon the reading. If the angle CAP $=\psi$ and POA $=\chi$, we have

$$\cos\theta = \sin\chi\cos\psi,$$

$$\tan\phi = \tan\chi\sin\psi,$$

and bending alters the value of ψ, so that the effect of bending is to produce

$$\delta\theta = \frac{\sin\chi\sin\psi}{\sin\theta}\,\delta\psi = 0 \text{ nearly}.$$

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* For the suggestion that I should investigate the effect of bending, I am indebted to Mr. E. G. Coker, Assist. Prof. of Civil Engineering, McGill University.

$$\delta\phi=\frac{\tan\chi\cos\psi}{\sec^2\phi}\delta\psi=\delta\psi \text{ nearly.}$$

So that the bending is added to the twist.

In the tests, however, a small load (250 lbs.) having been placed on the specimen, the bearings were tapped until the alignment had taken place. In pure torsion tests then the bending could have had no effect; and in the combined tests, as the torsion load was applied first and then the axial load, if the latter produced any bending it would alter the reading of the twist. On only one occasion was this of any magnitude, and usually the reading remained nearly constant until the yield-point was reached, when it increased. I therefore do not think that the source of error indicated above had an appreciable effect on the twist readings.

38. *As a Transmission Dynamometer.*—It may be noticed that in the case where the normals to the mirrors are perpendicular to the specimen, the reflected optical axis is turned through twice the angle the specimen twists through, and this relationship is exact. By using a ray of light of small cross section and allowing it, after reflexion at the two mirrors, to fall upon a scale, its position will indicate the twist between the mirrors; and since the reading can be taken when the light is intermittent, the device forms a cheap and convenient form of transmission dynamometer.

39. *The Diametral Extensometer.*—The diametral extensometer (fig. 14, p. 93) consists of a piece 1 resting in contact with the specimen at the surfaces A B C D forming parallel V's (as in the Adjuster); to this was hinged by an axis resting in two V's E, F, and a point at the end of the axis resting on a surface G, a lever 2. The lever 2 has a projection H which was kept in contact with the tube by a spring K. The piece 1 also carried the V-bearings L, M of a mirror-frame 3, the axis of the bearings being perpendicular to the axis of the specimen. The mirror-frame was connected to a screw working in the lever 2 by means of a link 4; the link having sharp knife-edges of V-form which worked on knife-edges on the screw and mirror-frame. The instrument was supported partly by springs, and partly by the friction at the surface of the tube. The distance of the knife-edge N

fastened to the mirror-frame, and upon which the link 4 worked, being small, its distance from the axis of rotation of the mirror-frame was determined by clamping the piece 1 and a micrometer-screw in such a way that turning the screw pushed, by means of a small distance-piece, the knife-edge through a definite amount. The twist of the mirror was then determined optically. The amount of the strain corresponding to any twist of the mirror can then be easily calculated ; it being remembered that, owing to the use of V's for the tube to rest in, the movement of H relative to the piece 1 is not simply the increase of the diameter, but is to be considered as the effect of an enlargement of the tube. If α is the semi-angle of the V's, the distance from the point of the V to the point of contact of the lever is $r(1+\operatorname{cosec}\alpha)$, where r is the radius of the tube. Hence an increase of radius δr corresponds to a movement of the lever at the point of contact with the tube of $\delta r(1+\operatorname{cosec}\alpha)$.

40. *Method of making the Tests.*—In making the tests, a tube, after its dimensions had been determined, was soldered on to the holders and then placed in the testing-machine, and a load of 250 lbs. applied, and the shackle-bearings tapped in order to make the specimen line itself up as accurately as possible. This load of 250 lbs. was employed as it pulled into contact the surface of the lower head of the testing-machine, which would not be in contact permanently until the load on the specimen exceeded the weight of all the parts between it and the straining-gear of the machine. [There was also a slight amount of backlash in the nut of the screw.] The torsion-bars and steel points were placed in their positions, and the screws in the bracket adjusted to just touch the lower cross-bar. The grips of the extensometer were then fixed to the specimen by the use of the adjuster, and the lower torsion-mirror applied. The telescope for the torsion-tests was then adjusted opposite the lower mirror with its optical axis horizontal, and the lower mirror was adjusted by the screws in its frame until the reflexion of the optical axis was parallel to the specimen. The top mirror was then fixed to the top grip and the torsion-scale placed at the same level : the screws of the top mirror were then adjusted until the image of the scale

appeared horizontal and at the centre of the field. The scale was then moved horizontally until the reading was nearly zero, the final adjustment to zero being made just before a test by the azimuth-screw of the telescope. The adjustment of the mirrors is such as to satisfy the condition found above (§ 36) for the vanishing of the terms of the second order in the expansion of the twist. The remaining parts of the extensometer were then placed in position, and the scale for axial extensions being moved so that its centre was opposite the mirror, the second screw Q was used to adjust the reading to nearly zero, the final adjustment being made by the altitude-screw of the corresponding telescope. The diametral extensometer was then adjusted on the specimen, above the other and strain apparatus.

The various forces were applied by suitable increments, and readings of the extensometer taken at each application: the time-effect at the elastic limit was looked for, and at its appearance the forces were applied by smaller amounts until it was judged that the yield-point had been reached. In tests involving tension and torsion the torque was applied first; during the application of the tension-load the first reading seldom changed appreciably, though it usually changed a few divisions. On only one occasion was the change (indicating a bending-moment) considerable. In all tests involving internal pressure, the pressure was applied last, as it was somewhat difficult to keep it constant at a desired amount. In the Tables the tension-loads are denominated by the letter P, and expressed in pounds-weight; the loads producing torque by W, so that the torques are 15 W inch-lbs., the cross-bar being 30 inches long between the points; the fluid pressure as recorded by the gauge by p_0, the corresponding pressure being obtained from the table of gauge corrections. The reading of the axial extensometer is called the axial reading, the factor to reduce this is changed in the course of the tests; otherwise all scales were placed at standard distances. This factor was 0·000001286 for tubes I., II., III., X., XI., XII., XIII., and 0·000001265 for the remainder. The reading to determine the twist is called the twist-reading; the factor to reduce it to shearing-strain or slide varies with the diameter of the tube, for a $1\frac{1}{4}$-inch diameter tube it is 0·00000377. The diametral extensometer readings have not been tabulated, it having been deemed more reliable to deduce the strain from the elastic constants; the factor to reduce scale-readings to strains was 0·000002022 for a $1\frac{1}{4}$-inch diameter tube. Examples of the results of this extensometer will be found plotted in some of the stress-strain curves (figs. 21, 23, & 24).

The values of P, W, p_0, the axial and the twist readings for the yield-point in the various tests are tabulated in Tables VI., VII., and VIII. under the head of observations.

41. *Determination of the Sectional Area and Thickness of the Tubes.*—The external diameter of the specimens was determined by the use of a micrometer-caliper; they were all practically uniform. The thickness was determined in every case by calipering, and also indirectly from the area of cross-section. The cross-section was determined in cases I., III., X., XI., XII., and XIII. by weighing the tubes in air and in water, the tubes being well boiled in the water, and the specific gravity of the water at the temperature checked. The density as well as the cross-section was thus determined. The other tubes were weighed and the thickness deduced from the result: as it always closely agreed with the makers' statement and with the result of direct measurement, the values may be regarded as fairly close. It should be noticed that errors in the thickness will only very slightly affect the relative results of the tests upon a tube, as the change in the mean diameter is the only way by which the relative results would be affected.

42. *Calculation of the Stresses.*—The effect of an axial force P is to produce a stress p, equal to the force divided by the area of the specimen: the values of these stresses for the various experiments are tabulated in the column headed p.

Owing to the smallness of the friction at the bearings, it has not been thought necessary to allow for it in the value of W; the cases which it affects most are those in which P is large and W comparatively small, the friction being practically proportional to P. The effect of a torque 15 W is to produce a shearing-stress q in the material of the tube varying from the inner surface to the outer proportionally to the distance from the axis. As the thickness of the tube is only from 0·04 to 0·06 of the radius, the variation of the shearing-stress from its mean value is only 2 or 3 per cent. The value of q is taken as equal to the torque divided by the product of the area of section and the mean radius. A simple shearing-stress q is equivalent to two principal stresses $+q$ and $-q$. It is to be noticed that neither tension, torsion, nor their combination produces a third principal stress.

The effect of the fluid pressure is to produce an axial stress p_1 and a circumferential stress whose mean value is $2p_1$, where $p_1 = \frac{\pi(r-t)^2}{\text{area}} \times$ fluid pressure; and a radial stress varying from the value of the fluid pressure at the interior surface to zero at the exterior surface.

Since in a cylinder under internal pressure the circumferential stress is given by the equation $p = \mathrm{C}\left(1+\frac{r_0^2}{r^2}\right)$, where r_0 is the external radius and r the radius at which the stress is p, the circumferential stress at the interior bears to that at the exterior the ratio $\frac{1}{2}\left(1+\frac{r_0^2}{(r_0-t)^2}\right) = 1+\frac{t}{r}$ nearly. Hence the variation from the mean value is about 2 or 3 per cent., as in the case of the shearing-stress due to torque.

In the calculations the mean values of the radius have been used, and no notice taken of the variation of the stress. In the hydraulic tests the actual amount of variation in pounds per sq. inch is equal to the value of the fluid pressure, since the sum of the radial and circumferential stresses is the same throughout the material of the cylinder.

The value of the axial stress due to the fluid pressure at the yield-point in the test is tabulated in the column headed p_1. In the case of a simultaneous tension-load producing an additional stress p_0, this is simply added on, so that the principal stresses are then $p+p_1$ axially, $2p_1$ circumferentially, and $\frac{1}{2}p_0$ radially.

To find the principal stresses when torsion is combined with tension or internal pressure, notice first that the radial stress is always perpendicular to the other components and to the plane of the shear, and hence it is a principal stress, and the case reduces to one of two dimensions and the stress ellipsoid to

$$p_1x^2+2qxy+p_2y^2=1,$$

where p_1, p_2 are the component axial and circumferential stresses and q the shearing-stress. The principal stresses ϖ_1, ϖ_2 are then the roots of the discriminant

$$\begin{vmatrix} p_1-\varpi & q \\ q & p_2-\varpi \end{vmatrix}=0;$$

and hence are the values of

$$\varpi=\frac{p_1+p_2\pm\sqrt{\overline{p_1-p_2}^2+4q^2}}{2}.$$

From this equation are obtained the tabulated values of ϖ_1 and ϖ_2. The angle at which the principal stresses are inclined to the generators may be found from its algebraic value $\tan^{-1}\dfrac{2q}{p_2-p_1}$.

In the tables of results the next column contains the maximum shearing-stress; this takes place in a plane perpendicular to the axis of mean principal stress, and is that of the plane through the mean axis bisecting the angles between the other principal stresses: its value is half the difference between the greatest and least principal stresses. It will be noticed in the case of those experiments in which the stresses in the tangential plane are of opposite signs, that this tangential plane is the plane of the greatest shear, but that in the other cases the plane passes through the axis of the tube. The value of the maximum shearing-stress in cases involving torsion is, from the value of the principal stresses, $\sqrt{\left(\dfrac{p_1-p_2}{2}\right)^2+q^2}$.

43. *Calculation of the Strains.*—Owing to the elastic-limit effect the measured strains vary more than the stresses, especially as the elastic-limit effect is practically absent in a test when the immediately preceding test is of the same type.

In the simple torsion tests the value of the shearing-strain or slide ϕ is obtained directly from the reading by the use of the factor. If i be the angle of twist of the specimen in a length l, r the radius of the specimen, d the distance to the scale, measured in the same units as x the scale-reading, we have

$$\phi=\frac{r}{l}i=\frac{r}{l}\frac{x}{d}.$$

The principal component strains which produce the slide ϕ are $\eta_1=\frac{1}{2}\phi$; $\eta_2=-\frac{1}{2}\phi$; and $\eta_3=0$.

The effect of an axial stress is not only to produce an axial strain, but to produce a uniform strain of the opposite sign in all directions at right angles to it, and bearing to it, in amount, the value of Poisson's ratio (σ). The value of the axial strain was determined from the corresponding scale-reading by the use of a factor; the value of the resulting contractile strain was obtained by multiplying this by the value of σ deduced from the values of E and C for the specimen, in preference to using the results of the diametral extensometer.

In the combined tension and torsion tests, the value of the principal strains was obtained from the observed value of the axial strain ϵ_1 and of the slide ϕ, and by taking the value of the circumferential strain as $-\sigma\epsilon_1$. Since ϕ is the only slide the strain ellipsoid becomes

$$\epsilon_1x^2+\epsilon_2y^2+\epsilon_3z^2+\phi xy=1,$$

where ϵ_2 and ϵ_3 are the strains perpendicular to ϵ_1. The discriminant then becomes

$$\begin{vmatrix} \epsilon_1-\eta & \frac{1}{2}\phi \\ \frac{1}{2}\phi & \epsilon_2-\eta \end{vmatrix}=0;$$

and the principal strains have the values

$$\tfrac{1}{2}\left\{\epsilon_1+\epsilon_2\pm\sqrt{(\epsilon_1-\epsilon_2)^2+\phi^2}\right\};\ \epsilon_3.$$

The maximum shear-strain, being the difference between the greatest and least principal stresses, is

$$\sqrt{(\epsilon_1-\epsilon_2)^2+\phi^2}.$$

In the case of the internal pressure experiments, the strains have been calculated from the values of the principal stresses and of the elastic constants. The results so obtained are always less than the measured values of the strains would be; as in the tension and internal pressure the axial strain is a principal one, its measured volume in the column "Axial strain" can be compared with its calculated value in the column η_1 of the principal strains.

The maximum slides or shear-strains, being in value equal to the difference between the greatest and least principal strains, have also been tabulated ; these should be, but for the elastic-limit effect, directly proportional to the maximum shearing-stresses, and independent of the third stress.

44. *Maximum Shear and Slide are proportional.*—For if the principal stresses be $\varpi_1, \varpi_2, \varpi_3$, then the maximum shearing-stress perpendicular to ϖ_3 is $\frac{1}{2}(\varpi_1 - \varpi_2)$. The principal strains are $\frac{1}{E}(\varpi_1 - \sigma\varpi_2 - \sigma\varpi_3), \frac{1}{E}(\varpi_2 - \sigma\varpi_3 - \sigma\varpi_1), \frac{1}{E}(\varpi_3 - \sigma\varpi_1 - \sigma\varpi_2)$, and the corresponding maximum slide to $\frac{1}{2}(\varpi_1 \quad \varpi_2)$ is $\frac{1+\sigma}{E} \times (\varpi_1 - \varpi_2)$. So that the maximum slide directly corresponds to the maximum shearing-stress and is independent of the stress normal to its plane. Thus the comparison of the maximum shear and slide columns in the tables of results will indicate the magnitude of the elastic-limit effect.

45. *Quantities tabulated.*—Thus for the tests the values of the principal stresses, of the principal strains, of the maximum shear, and the maximum slide at the yield-point have been tabulated ; a column has also been included giving the maximum principal strain as calculated from the elastic constants and stresses, this being the yield-point strain on the supposition that Hooke's law holds up to the yield-point.

The values of E, Young's modulus, and C, the modulus of rigidity, have been calculated from the elastic ratio of stress and strain in the tension and torsion experiments ; they have slight variations for the same tube. The value of σ, Poisson's ratio, has been deduced from these by the formula $\sigma = \frac{E}{2C - E}$, which is a method evidently liable to large errors ; these, however, I do not think are serious enough to affect the conclusions I have drawn from the tables of results, as the chief conclusions are deduced from the stresses. I had intended to deduce the value of σ directly from the internal pressure tests; the axial elongation due to a pressure p_0, producing stresses p_1 and $2p_1$, being $\frac{p_1}{E}(1-2\sigma)$, so that $\sigma=0{\cdot}5-\frac{E}{2p_1}\times$ (axial strain). The method of attaching the tube conveying the oil to the specimen was not perfect, and seemed to tilt the tube slightly as a whole, so that this method was not used. Perhaps Regnault's method would have been most appropriate.

The results of the experiments are given in Tables V. (Solid Bars), VI. (Steel Tubes), VII. (Copper Tubes), and VIII. (Brass Tubes), where the observations made at the yield-point and the results will be found.

46. *Results of the Experiments.*—For the more ready presentation of the results of the experiments, diagrams of various types have been drawn, and will be described as referred to.

The Tests on Solid Bars.—In the case of the solid-bar tests it will be observed that the yield-point stresses (see Table V.) rise as the course of tests proceeds: this indicates that the yield-point of the outer layers must have been much exceeded (§ 5). A glance at the torque-twist diagram (fig. 15) for the torsion-tests will clearly demonstrate the difficulty of locating the yield-point; though the tables merely embody my estimations of its occurrence, the curves at any rate represent actual occurrences, and permit of the ready comparison of points considered to correspond. The results may be held, with previous torsion experiments, to disprove the maximum-stress theory, as the ratios of the maximum stresses in the torque and tension tests are 0·615 to 0·69 for the iron, and 0·565 for the steel. They are also at variance with the maximum-strain theory, the values of the ratio for the experimental values of σ being 0·75 and 0·71 respectively. In this and some of the succeeding figures the time-effect is shown by observations giving different strains under a constant stress; the first observations were taken immediately the loads were applied; in some cases the intervals of time are given.

SYNOPSIS OF TUBE-TESTS.

NOTATION.

The tests on any tube are numbered in order of performance.
All results refer to the yield-point.
P =actual tension-load on specimen.
W=load producing the torque 15 W.
p_0 =corrected value of internal pressure.
Axial-strain=actual reading of the axial extensometer-scale.
Twist-strain= ,, ,, twist-scale.
p =the tensile-stress due directly to P.
q =the shearing-stress due directly to W.
p_1=the axial stress due directly to p_0.
ϖ_1, ϖ_2, ϖ_3=the principal stresses.
Axial strain as measured=the value of the strain as deduced from the reading of the axial scale.
Twist-strain as measured=the value of the slide as deduced from the reading of the twist-scale.
η_1, η_2, η_3 are the principal strains.

TABLE IV.

Diameters, Elastic Constants, &c. of Tubes.

No. of Tube.	Material.	Diam.	Thickness.	Area.	E.	C.	σ.
I.	Steel	1·316	0·029	0·1175	30,400,000	10,960,000	0·39
II.	,, ...	1·250	0·028	0·1075	29,500,000	11,450,000	0·287
III.	,, ...	0·4987	0·0245	0·0364	28,900,000	10,660,000	0·355
IV.	,, ...	1·25	0·025	0·0971	31,100,000	11,170,000	0·393
V.	,, ...	,,	,,	,,	31,700,000	11,700,000	0·355
VI.	,, ...	,,	,,	,,	30,900,000	11,500,000	0·344
VII.	,, ...	,,	,,	,,	28,800,000	10,850,000	0·328
VIII.	,, ...	,,	,,	,,	31,000,000	11,200,000	0·365
IX.	,, ...	,,	,,	,,	29,600,000	10,400,000	0·423
X.	Copper ...	1·251	0·0362	0·14113	18,100,000	6,280,000	0·43
XI.	,, ...	,,	,,	,,	17,200,000	6,000,000	0·43
XII.	Brass	1·255	0·034	0·1295	15,000,000	5,020,000	0·45*
XIII.	,, ...	,,	,,	,,	14,760,000	4,760,000	0·50

The units for the above table are lbs. wt. and inches.

Solid Bars, Elastic Constants, &c.

Material.	Diam.	Area.	E.	C.	σ.
Norwegian Iron ...	0·628	0·3095	29,700,000	11,160,000	0·33
Mild Steel............	0·504	0·1992	31,800,000	11,270,000	0·40

TABLE V.—Solid Bar Tests.

Elastic Limit.

Material.	Test No.	P.	W.	p.	q.	Max. Shear.	Max. Elongation.
Norwegian Iron .	1	...	30	...	9,000	9,000	0·000403
,, ...	2	5000	...	16,200	...	8,100	0·000554
,, ...	3	5000	20	16,200	6,180	10,200	0·00064
,, ...	4	6700	30	21,700	9,270	14,300	0·00088
,, ...	5	8000	...	26,000	...	13,000	0·00083
,, ...	6	...	48	...	14,800	14,800	0·000665
Mild Steel	1	...	22	...	13,100	13,100	0·000582
,, ...	2	6750	...	33,900	...	16,950	0·001065
,, ...	3						

Yield-point.

Material.	Test No.	P.	W.	p.	q.	Max. Shear.	Max. Elongation.
Norwegian Iron .	1	...	40	...	12,360	12,360	0·00055
,, ...	2	6400+	...	20,700	...	10,350	0·000698
,, ...	3	5000	42½	16,200	13,100	15,300	0·00087
,, ...	4						
,, ...	5	8200	...	26,500	...	13,250	0·000892
,, ...	6	...	59	...	18,200	18,200	0·000815
Mild Steel	1	...	38	...	22,700	22,700	0·001007
,, ...	2	8000	...	40,200	...	20,100	0·001265
,, ...	3	6000	35	30,100	20,900	25,800	0·00142

The above elongations are calculated from the stresses and elastic constants, thus assuming that the linear stress-strain relation holds to the yield-point; the actual strains at the yield-point are greater: *e.g.*, the max. elongation at W=40 in Test 1 on the Norwegian iron was at first 0·000587 and increased to 0·000606.

Table VI.—Results of Tests. Steel Tubes.

Number of		OBSERVATIONS.					CALCULATED STRESSES.							CALCULATED STRAINS.						Maximum Elongation as calculated from Stresses.
		Stress.			Strain.		Applied.			Principal.			Max. Shear.	As measured.		Principal.			Maximum Slide.	
Tube.	Test.	P.	W.	p_0.	Axial.	Twist.	p.	q.	p_1.	ϖ_1.	ϖ_2.	ϖ_3.		Axial.	Twist.	η_1.	η_2.	η_3.		
I.	1...	...	88	...	...	91·5	0	17,900	...	17,900	−17,900	0	17,900	...	0·001665	0·000832	−0·000832	0	0·001665*	0·000817
	2...	5380	...	450	2281	...	45,800	...	4,500	50,300	9,000	0 to −430	25,360	0·00155	...	0·00155	...	...	...	0·001540
	3...	5200	...	680	2266	...	44,300	...	6,750	51,050	13,500	0 to −640	25,840	0·00154	...	0·00154	...	...	...	0·001510
	4...	5160	...	730	2154	...	43,900	...	7,400	51,300	14,800	0 to −700	26,000	0·00147	...	0·00147	...	...	...	0·001500
	5...	5500	...	..	2258	...	46,800	...	...	46,800	0	0	23,400	0·00154	...	0·00154	...	...	...	0·001540
	6...	...	88	...	...	66·0	...	17,900	...	17,900	−17,900	0	17,900	...	0·00197	0·000985	−0·000985	0	0·001970	0·000817
II.	1...	150	135–150	...	...	680–785	...	30,800 to 34,200	...	30,800 to 34,200	−30,800 to −34,200	0	34,200	...	0·00263 to 0·00304	0·00131 to 0·00152	−0·00131 to −0·00152	3	0·00263 to 0·00304	0·00142
	2...	6500+	...	...	1582+	...	60,500+	...	...	60,500+	0	0	30,250+	0·002032	...	0·002032	−0·000583*	−0·000583*	0·002615*	0·002050
	3...	200	130	...	...	696	...	29,500	...	29,500	−29,500	0	29,500	...	0·00269	0·00134	−0·00134	0	0·00269	0·00129
	4...	4200	...	...	1026	...	39,100	...	...	39,100	0	0	18,550	0·00132	...	0·00132	−0·000379*	−0·000379*	0·00170	0·001320
	5...	3700	100	some bending	920	527	34,500	22,800	...	45,800	−11,350	0	28,600	0·001132	0·00204	0·001691	−0·000848	−0·000339*	0·00254	0·00168
	6...	5950	...	...	1600	...	55,500	...	...	55,500	0	0	27,750	0·002055	...	0·002055	−0·000732*	−0·000732*	0·002787*	0·001880
	7...	6200	...	...	1575	...	57,800	...	...	57,800	0	0	28,900	0·002025	...	0·002055	−0·000645*	−0·000645*	0·002670*	0·001960
	8...	5200	75	...	1450	440	48,500	17,100	...	53,900	− 5,400	0	29,650	0·001865	0·001703	0·002135	−0·000805	−0·000535*	0·00294	0·001775
	9...	250	130	...	...	798	...	29,500	...	29,500	−29,500	0	29,500	...	0·00309	0·00154	−0·00154	0	0·00309	0·001290
	10...	4200	100	...	885	560	39,100	22,800	...	49,900	−10,800	0	30,350	0·001137	0·002165	0·001710	−0·000899	−0·000326*	0·002610	0·001830
	11...	4000	110	...	1074	644	37,200	25,100	...	49,800	−12,600	0	31,200	0·001383	0·002490	0·001998	−0·001012	−0·000397*	0·00301	0·001810
	12...	4500	...	1050	1160	...	41,90	...	11,000	52,900	22,000	0 to 1050	27,000	0·001491	...	0·001491	−0·000428	−0·000428	0·001919	0·001545
III.	1...	50	9	...	..	948	...	15,650	...	15,650	−15,650	0	15,650	...	0·001427	0·000714	−0·000714	0	0·001328	0·000735
	2...	1250	...	...	946	...	34,400	...	...	34,400	0	0	17,200	0·001217	...	0·001217	−0·000432*	−0·000432*	0·001649*	0·001190
	3...	50	9	...	...	1039	...	15,650	...	15,650	−15,650	0	15,650	..	0·001567	0·000783	−0·000783	0	0·001567	0·000735
	4 ..	750	7	...	566	752	20,600	12,150	...	26,250	5,650	0	15,950	0·000727	0·001133	0·000977	−0·000518	−0·000258	0·001505	0·000977
	5 ..	1000	5	...	750	536	27,500	8,680	...	30,050	2,550	0	16,300	0 000342	0·000808	0·001078	−0·000456	−0·000342	0·001535	0·001070
	6...	1200	...	....	895	...	33,000	...	...	33,000	0	0	16,500	0·001152	...	0·001152	−0·000408	−0·000408	0·001560	0·001140
IV.	1...	...	90	...	...	550	...	22,500	...	22,500	−22,500	0	22,500	...	0·002070	0·001035	−0·001035	0	0·002070	0·001005
	2...	4000	...	...	1094	...	41,200	...	...	41,200	0	0	20,600	0·001385	...	0·001385	−0·000545	−0·000545	0·001930	0·001325
	3...	2750	70	...	814	450	28,300	17,500	...	38,650	−8,350	0	22,500	0·001030	0·001695	0·001425	−0·000800	−0·000405	0·002220	0·001350
	4...	3000	...	1150	911	...	30,900	...	12,000	42,900	24,000	0 to −1050	22,000	0·001152	...	0·001075	0·000230	−0·000845	0·001920	0·001078
	5...	...	75	1150	104	454	...	18,750	12,000	37,700	−1,700	0 to −1050	20,200	0·000132	0·001710	0 001250	−0·000546	−0·000455	0·001795	0·001235
	6...	2500	...	1600	900	...	25,800	...	16,900	42,700	33,800	0 to −1500	22,100	0·001138	...	0·000940	0·000547	−0·000975	0·001915	0·000975
	7...	3400	50	...	948	303	35,000	12,500	...	39,000	−4,000	0	21,500	0·001200	0·001140	0·001324	−0·000656	−0·000472	0·001980	0·001305
	8...	4000	...	...	1097	...	41,200	...	...	41,200	0	0	20,600	0·001388	...	0·001388	−0·000545	−0·000545	0·001933	0·001325
	9...	...	90	...	...	561	...	22,500	...	22,500	−22,500	0	22,500	...	0·00214	0·000107	−0·000107	0	0·00214	0·001005

V.	1...	3250	...	...	949	...	33,500	...	...	33,500	0	0	16,750	0·001200	...	0·001200	−0·000426	−0·000426	0·001626	0·001057
	2...	250	70	..	...	419	2,600	17,500	...	17,500	−17,500	0	17,500	...	0·001580	0·000790	−0·000790	0	0·001580	0·000748
	3...	2600	45	...	725	274	26,800	11,250	...	30,900	−4,100	0	17,500	0·000917	0·001032	0·001191	−0·000599	−0·000325	0·001790	0·001620
	4...	3200	...	...	889	...	33,000	...	...	33,000	0	0	16,500	0·001125	...	0·001125	−0·000400	−0·000400	0·001425	0·000104
	5...	2800 to 3000	35	...	754	242	30,800	8,750	...	33,100	−2,300	0	17,700	0·000955	0·000912	0·001100	−0·000484	−0·000339	0·001585	0·000107
	6...	2000	...	1200	780	...	20,600	...	12,000	32,600	24,000	0 to −1050	16,800	0·000987	...	0·000760	+0·000393	−0·000633	0·001393	0·000760
	7...	...	45	1150	150	380	...	11,250	12,000	30,500	5,500	0 to −1050	15,750	0·000190	0·001431	0·000900	−0·000167	−0·000403	0·001510	0·000900
	8...	1500	...	1425	626	...	15,450	...	14,900	30,350	29,800	0 to −1350	15,9 0	0·000792	...	0·000625	0·000602	−0·000673	0·001298	0·000673
	9...	250	70	...	...	643	2,600	17,500	...	17,500	−17,500	0	17,500	...	0·002425	0·001212	−0·001212	0	0·002425	0·000748
	10...	3300	...	...	1418	...	34,000	...	...	34,000	0	0	17,000	0·001793	...	0·001793	−0·000637	−0·000637	0·0024 0	0·001073
VI.	1...	3300	...	...	1440	...	34,000	...	...	34,000	0	0	17,000	0·001822	...	0·001822	−0·000612	−0·000612	0·002434	0·001100
	2...	3300	...	...	971	...	34,000	...	...	34,000	0	0	17,000	0·001230	...	0·001230	−0·000412	−0·000412	0·001642	0·001100
	3...	2000	...	1175	686	...	20,600	...	12,300	32,900	24.600	0 to −1100	17,000	0·000867	...	0·000792	0·000431	−0·000640	0·001432	0·000792
	4...	2500	...	900	747	...	20,800	...	9,450	30,250	18,900	0 to −850	15,550	0·000945	...	0·000768	0·000275	−0·000548	0·001316	0·000768
	5...	250	65	...	...	524	2,600	16,250	...	16,250	−16,250	0	16.250	...	0·001975	+0·000987	−0·000987	0	0·001975	0·000705
	6...	3000	35	...	985	240	30,900	8,750	..	33,150	−2,250	0	17,770	0·001245	0·000905	0·001359	−0·000531	−0·000417	0·001890	0·001100
	7...	2700	45	...	778	333	27,800	11,250	...	31,800	−4,000	0	17.900	0·000985	0·001255	0·001235	−0·000589	−0·000339	0·001825	0·001075
	8...	...	69	some bending.	...	554	...	17,250	...	17,250	−17,250	0	17,250	...	0·002085	0·001042	−0·001042	0	0·002085	0·000750
	9...	2550	50	...	714	347	26,300	12,500	...	31,250	−4,950	0	18,100	0·000904	0·001310	0·001189	−0·000596	−0·000311	0·001786	0·001065
	10...	1500	...	1125?	?	...	15,450	...	11,700	27,150	23,400	0 to −1050	14,100							
	11...	2000	...	1175	750	...	20,600	...	12,300	32,900	24,600	0 to −1100	17,600	0·000948	...	0·000792	0·000431	−0·000640	0·001432	0·000792
	12...	1500	...	1400	590	...	15,450	...	14,650	30,100	29,300	0 to −1300	15,700	0·000746	...	0·000648	0·000612	−0·000662	0·001310	0·000648
VII.	1...	1500	...	1800	? 500	...	15,450	...	18,900	34,350	37,800	0 to −1700	19,750	0·000633	...	0·000765	0·000925	−0·000821	0·001744	0·000925
	2...	2000	...	1650	715	...	20,600	...	17,450	38,050	34,900	0 to −1570	19,800	0·000905	...	0·000926	0·000781	−0·000830	0·001756	0·000926
	3...	2000	75	...	...	550	20,600	17,500	...	30,600	−5,000	0	20,300	...	0·002070	0·001355	−0·000870	−0·000237	0·002225	0·001130
	4...	...	60	1400	100	474	...	15,000	14,650	38,800	5,200	0 to −1300	20,050	0·000126	0·001785	0·001501	−0·000480	−0·000500	0·001960	0·001501
	5...	3800	...	...	1216	...	39,200	...	...	39,200	0	0	19,600	0·001540	...	0·001540	−0·000505	−0·000505	0·002045	0·001360
	6...	...	90	...	...	607	...	22,500	...	22,500	−28,500	0	22,500	...	0·002385	0·001192	−0·001192	0	0·002385	0·001035
	7...	2600	70	...	798	555	26,800	17,500	...	35,400	−8,600	0	22,000	0·001010	0·002090	0·001549	−0·000870	−0·000331	0·002420	0·001325
	8...	3400	50	...	1012	370	35,000	12,500	...	39,000	−4,000	0	21,500	0·001280	0·001395	0·001530	−0·000670	−0·000420	0·002200	0·001400
	9...	1500	...	1850	620	...	15,450	...	19,500	34,950	39,000	0 to −1750	20,400	0·000785	...	0·000772	0·000958	−0·000842	0·001800	0·000958
	10...	250	...	1900	? 162	...	2,600	...	19,900	22,500	39,800	0 to −1800	20,800	0·000205	...	0·000205	0·001128	−0·000710	0·001835	0·001128
	11...	500	...	1900	208	...	5,150	...	19,900	25,050	39,800	0 to −1800	20,800	0·000263	...	0·000417	0·001100	−0·000740	0·001840	0·001100
	12...	1000	...	1900	240	...	10,300	...	19,900	30,200	39,800	0 to −1800	20,800	0·000304	...	0·000596	0·00104	−0·000798	0·001838	0·001040
	13...	2000	...	1700	? 914	...	20,600	...	17,900	38,500	35,800	0 to −1600	20,050	0·001155	...	0·000930	0·000807	−0·000846	0·001776	0·000930
	14...	2500	...	1425	932	...	25,750	...	15,000	40,750	30,000	0 to −1350	20.900	0·001180	...	0·001075	0·000588	−0·000798	0·001873	0·001075
	15...	1500	...	1900	565	...	15,450	...	19,900	35,350	39,800	0 to −1800	20,800	0·000715	...	0·000773	0·000982	−0·000857	0·001839	0·000982
	16...	3700	...	...	1567	...	38,100	...	...	38,100	0	0	19,050	0·001980	...	0·001980	−0·000650	−0·000650	0·002630	0·001325
	17...	3600	25	...	1115	245	37,100	6,250	...	38,800	−1,700	0	20,250	0·001410	0·000920	0·001518	−0·000571	−0·000463	0·002090	0·001365
	18...	3500	40	...	1137	404	36,100	10,000	...	38,700	−2,570	0	20,600	0·001437	0·001520	0·001703	−0·000738	−0·000472	0·002440	0·001375
	19...	3100	60	...	1091	615	31,900	15,000	...	37,800	−5,900	0	21,900	0·001380	0·002315	0·001921	−0·000994	−0·000453	0·002915	0·001380
	20...	...	89	...	...	660	...	22,250	...	22,250	−22,250	0	22,250	...	0·002485	0·001242	−0·001242	0	0·002485	0·001025

TABLE VI. (*continued*).

Number of		OBSERVATIONS.					CALCULATED STRESSES.							CALCULATED STRAINS.						Maximum Elongation as calculated from Stresses.
		Stress.			Strain.		Applied.			Principal.			Max. Shear.	As measured.		Principal.			Max. Slide.	
Tube.	Test.	P.	W.	p_0.	Axial.	Twist.	p.	q.	p_1.	ϖ_1.	ϖ_2.	ϖ_3.		Axial.	Twist.	η_1.	η_2.	η_3.		
VIII.	1...	...	88·5	...	...	535	...	22,100	...	22,100	−22,100	0	22,100	...	0·00202	0·00101	−0·00101	0	0·00202	0·000985
	2...	...	89	...	...	563	...	22,250	...	22,250	−22,250	0	22,250	...	0·00212	0·00106	−0·00106	0	0·00212	0·001005
	3...	3900	...	...	1184	...	40,200	...	...	40,200	0	0	20,100	0·00150	...	0·00150	−0·00055	−0·00055	0·00205	0·001300
	4...	3300	50	...	899	318	34,000	12,500	...	38,125	− 4,125	0	21,150	0·001135	0·00120	0·00134	−0·00062	−0·000413	0·00196	0·00128
	5...	2600	70	...	696	448	26,800	17,500	...	35,400	− 8,600	0	22,000	0·00088	0·00169	0·001318	−0·00076	−0·00032	0·002075	0·00124
	6...	2500	...	1500	1004	...	25,750	...	15,750	41,500	31,500	0 to −1420	21,450	0·00127	...	0·00109	0·00060	−0·00086	0·00195	0·00109
	7...	2000	...	1700	733	...	20,600	...	17,900	38,500	35,800	0 to −1600	20,050	0·000926	...	0·00082	0·00070	−0·00087	0·00169	+0 00082 or −0·00087
	8...	1000	...	1875	474	...	10,300	...	19,650	29,950	39,300	0 to −1770	20,500	0·00060	...	0·00050	0·00092	−0·00081	0·00171	0·00092
	9...	500	...	1900	335	...	5,150	...	19,900	25,050	39,800	0 to −1795	20,800	0·000425	...	0·00034	0·00099	−0·00071	0·00170	0·00099
	10...	3000	...	1300	1124	...	30,900	...	13,500	44,400	27,000	0 to −1220	22,800	0·00142	...	0·00112	0·00035	−0·00084	0·00196	0·00112
	11...	1500	...	1850	588	...	15,450	..	19,600	35,050	39,200	0 to −1755	20,500	0·000745	...	0·00067	0·00086	−0·00087	0·00173	−0·00087
	12...	500	...	1950	347	...	5,150	...	20,500	25,650	41,000	0 to −1745	21,400	0·000438	...	0·000345	0·00102	−0·00078	0·00180	0·00102
	13...	250	...	over2000	284	...	2,575	...	20600+	23,175	41200+	0 to −2000	21,600	0·00036	..	0·00026	0·00106	−0·00076	0·00182	0·00106
	14...	1000	...	2025	556	...	10,300	...	21,300	21,600	42,600	0 to −1920	22,250	0·000705	...	0·00020	0·00112	−0·00076	0·00188	0·00112
	15...	2500	...	1550	1089	...	25,750	...	16,300	42,050	32,600	0 to −1470	21,750	0·001375	..	0·00097	0·000555	−0·00088	0·00185	0·00097
	16...	3500	...	900	1251	...	36,100	...	9,450	45,500	18,900	0 to −850	23,200	0·001585	...	0·00125	0·00007	−0·00076	0·00201	0·00125
	17...	2000	...	1850	870	...	20,600	...	19,600	40,200	39,200	0 to −1755	20,975	0·001100	...	0·00084	0·00080	−0·00093	0·00177	−0·00093
	18...	3000	...	1450	1206	...	30,900	...	15,200	46,100	30,400	0 to −1370	23,750	0·001525	...	0·00113	0·00044	−0·00090	0·00203	0·00113
	19...	? 4000	...	...	1526	...	41,200	...	...	41,200	0	0	20,600	0·00193	...	0·00193	−0·0007	−0·0007	0·00263	0·00133
	20...	500	85	...	...	702	5,150	21,250	...	21,250	−21,250	0	21,250	...	0·00265	0·00137	−0·00137	0	0·00265	0·00095
IX.	1 ...	...	...	1600	355	...	...	...	16,900	16,900	33,800	0 to −1520	17,650	0·000448	...	0·000088	0·000900	−0·000725	0·001625	0·000900
	2 ...	3300	...	...	1367	...	34,000	...	...	34,000	0	0	17,000	0·001730	...	0·001730	−0·000767	−0·000767	0·002497	0·001150
	3 ...	3500	...	...	950	...	36,000	...	...	36,100	0	0	18,050	0·001202	...	0·001202	−0·000533	−0·000533	0·001735	0·001220
	4 ...	...	80	...	...	633	...	20,000	...	20,000	−20,000	0	20,000	...	0·002390	0·001195	−0·001195	0	0·002390	0·00096
	5 ...	2500	60	..	798	435	25,750	15,000	...	32,670	− 6,900	0	19,800	0·001010	0·001640	0·001437	−0·000667	−0·000239	0·002094	0·001200
	6 ...	2500	...	1000	840	..	25,750	...	10,350	36,100	20,700	0 to −935	18,500	0·001062	...	0·000925	0·000184	−0·000812	0·001737	0·000925

TABLE VII.

Results of Tests.—Copper Tubes.

Number of		OBSERVATIONS.					CALCULATED STRESSES.							CALCULATED STRAINS.						
		Stress.			Strain.		Applied.			Principal.			Max. Shear.	As Measured.		Maximum Principal Strain calculated from Stresses.	Principal.			Max. Slide.
Tube.	Test.	P.	W.	p_0.	Axial.	Twist.	p.	q.	p_1.	ϖ.	ϖ_2.	ϖ_3.		Axial.	Twist.		η_1.	η_2.	η_3.	
X.	1 ...	...	35	...	...	378	...	6,070	...	6,070	—6,070	0	6,070	...	0·001425	0·000483	0·000712	—0·000712	0	0·001425
	2 ...	1500	...	...	612	...	10,630	...	...	10,630	0	0	5,315	0·000786	...	0·000588	0·000786	—0·000432	—0·000432	0·001218
	3 ...	1300	25	...	530	291	9,210	4,370	...	10,950	—1,755	0	6,360	0·000682	0·001095	0·000647	0·000910	—0·000525	—0·000297	0·001435
	4 ...	900	..	700	438	...	6,380	...	5,120	11,500	10,240	0 to —660	6,075	0·0005 63	...	—0·000523	0·000393	0·00029	—0·000523	0·000910
	5 ...	600	...	900	327	...	4,250	...	6,580	10,830	13,160	0 to —850	7,000	0·000420	...	—0·000478	0·00038	0·000468	—0·000478	0·000946
	6 ...	1700	...	...	662	...	12,050	...	...	12,050	0	0	6,025	0·000850	...	0·000665	0·000850	—0·00037	—0·00037	0·00122
	7 ...	1800	...	...	606	...	12,750	...	...	12,750	0	0	6,375	0·000780	...	0·000705	0·00780	—0·00034	—0·00034	0·00112
	8 ...	...	35	...	...	3 41	...	6,070	...	6,070	—6,070	0	6,070	...	0·001285	0 000483	0·000642	—0·000642	0	0·001285
	9 ...	...	25	800	115	255	...	4,370	5,730	13,835	3,355	0 to —740	7,300	0·000148	0·000962	0·000685	—0·00015	0·000685	—0·000412	0·001097
XI.	1 ...	...	...	825	136	...	...	...	5,925	5,925	11,850	0 to —750	6,300	0·000175	...	0·000515	0·000045	0·000515	—0·000423	0·000938
	2 ...	1400	...	...	464	...	9,925	...	...	9,925	0	0	4,962	0·000595	...	0·000577	0·000595	—0·00026	—0·00026	0·000855
	3 ...	1250	...	525	525 ?	...	8,860	...	3,870	12,730	7,740	0 to —500	6,600	0·000675 ?	...	0·00052	0·00052	0·00012	—0·00049	0·00100
	4 ...	...	35	...	...	436	...	6,070	...	6,070	—6,070	0	6,070	...	0·00164	0·000505	0·00082	—0·00082	0	0·00082

Table VIII.

Results of Tests.—Brass Tubes.

Number of		OBSERVATIONS.					CALCULATED STRESSES.							CALCULATED STRAINS.						
Tube.	Test.	Stress.			Strain.		Applied.			Principal.			Max. Shear.	As Measured.		Maximum Principal Strain calculated from Stresses.	Principal.			Max. Slide.
		P.	W.	p_0.	Axial.	Twist.	p.	q.	p_1.	ϖ_1	ϖ_2.	ϖ_3.		Axial.	Twist.		η_1.	η_2.	η_3.	
XII.	1 ...	50	52·5	...	...	574	..	9,450	...	9,450	− 9,450	0	9,450	...	0·00216	0·000940	0·00108	−0·00108	0	0·00216
	2 ...	2250	...	...	1070	...	17,400	...	...	17,400	0	0	8,700	0·001375	...	0·001160	0·001375	−0·00055	−0·00055	0·001925
	3 ...	2000	25	...	892	244	15,450	4,500	..	16,650	− 1,215	0	8,940	0·001145	0·000918	0·001145	0·001267	−0·000582	−0·00046	0·001850
	4 ...	1600	40	...	748	438	12,370	7,200	...	14,685	− 2,315	0	8,500	0·000962	0·00165	0·001045	0·001353	−0·000776	−0·000385	0·00213
	5 ...	1750	...	900	857	...	13,520	...	7,250	20,770	14,500	0 to −850	10,800	0·001100	...	0·001075	0·001075	0·000446	−0·001013	0·00209
	6 ...	1500	...	950	763	...	11,580	...	7,680	19,260	15,360	0 to −900	10,075	0·000980	...	−0·000995	0·000945	0·000550	−0·000995	0·00194
	7 ...	2600	...	...	1087	...	20,100	...	...	20,100	0	0	10,050	0·001398	...	0·00134	0·001398	−0·000685	−0·000685	0·002083
	8 ...	...	57½	...	...	645	...	10,350	...	10,350	−10,350	0	10,350	...	0·00243	0·00103	0·00116	−0·00116	0	0·00243
	9 ...	1900	40	...	820	480	14,670	7,200	...	17,610	− 2,940	0	10,275	0·001053	0·00181	0·001265	0·001485	−0·000854	−0·000422	0·00234
	10 ...	1500	...	1050	661	...	11,580	...	8,400	19,980	16,800	0 to −985	10,525	0·000850	...	−0·00121	0·00078	−0·000465	−0·00121	0·00199
	11 ...	1800	...	900	784	...	13,900	...	7,250	21,150	14,500	0 to −850	11,000	0·001005	...	−0·00116	0·00093	0·000272	− 0·00116	0·00209
	12 ...	...	45	825	118	528	...	8,100	6,520	18,520	1,040	0 to −750	9,100	0·000152	0·00199	0·00120	+0·00120	−0·000534	−0·000636	0·00184
XIII.	1 ...	1500	...	950	759	...	11,580	...	7,670	19,250	15,340	0 to −900	10,075	0·000975	...	−0·00115	0·000400	0·00080	−0·00115	0·00195
	2 ...	2300	...	...	1042	...	17,750	...	...	17,750	0	0	8,875	0·001340	...	0·001205	0·001340	− 0·00067	−0·00067	0·00201
	3 ...	350	45	...	...	480	...	8,100	...	8,100	− 8,100	0	8,100	...	0·00181	0·000850	0·00090	−0·00090	0	0·00181

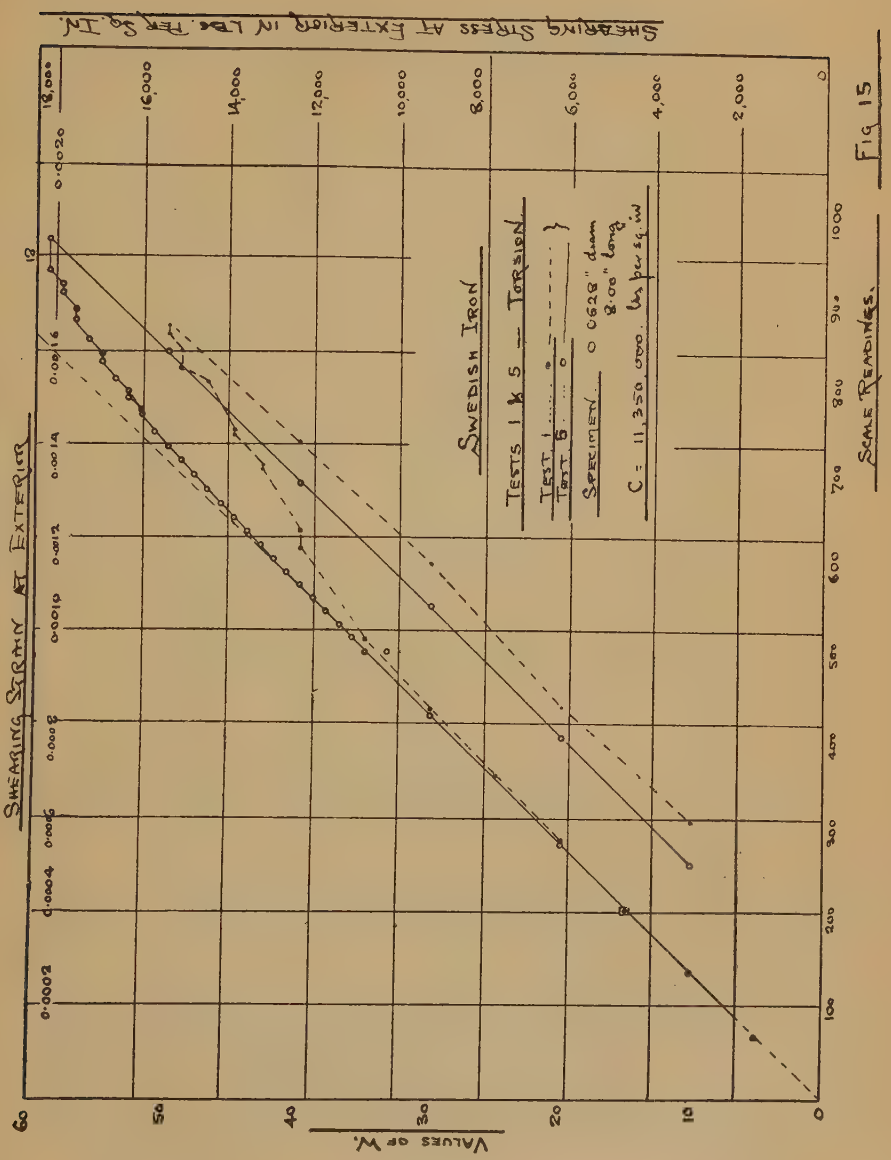


Fig. 15.—Torque Twist Curves for Solid Bar.

47. *The Material and Shape of Tubes satisfactory.*—Turning now to the results of the tube-tests, reference to Table IV. will show that the densities found were high, and that the values of the moduli of elasticity are usual values for the various materials, and certainly not low; also inspection of various stress-strain diagrams indicates that the relation is linear up to a considerable fraction of the yield-point stress. For these reasons the tubes may be taken as of sufficient excellence in material and shape to afford results worthy of consideration.

Few torsion-internal pressure experiments have been performed, but a comparison of results obtained thus with the results of those tests when somewhat similar stresses are differently produced, will tend to cause confidence in the experiments. The torsion-internal pressure tests are Nos. IV. 5, V. 7, VII. 4, X. 9, and XII. 12.

48. *The Elastic-limit Phenomenon.*—The elastic-limit phenomenon, it will be observed, is much decreased in a repetition of a test, the observed strain at the yield-point being less in the second test than in the first, although the stress-strain curves within the elastic limit practically coincide. To illustrate this point some of the tests bearing upon it have been plotted out observation by observation; in figs. 16 and 17 are two sets of tension tests, and in fig. 18 some torsion tests.

When, however, a test imposes upon the material stresses of a different type to those of the preceding test, the elastic-limit effect, which may have temporarily disappeared owing to the similarity of the two preceding tests, is displayed to the full.

Copper seems, however, to harden so much under successive tests, that the strains appear as a whole to lessen with the amount of treatment.

The elastic-limit effect also increases with the number of times different stresses have been applied to the material, as may be seen by comparing the stress-strain curves for tests of the same type, but separated by a number of other tests. Examples are represented in figs. 16 (tension) and 18 (torsion).

This phenomenon may indicate that the cause of failure under comparatively low varying stresses, such as employed

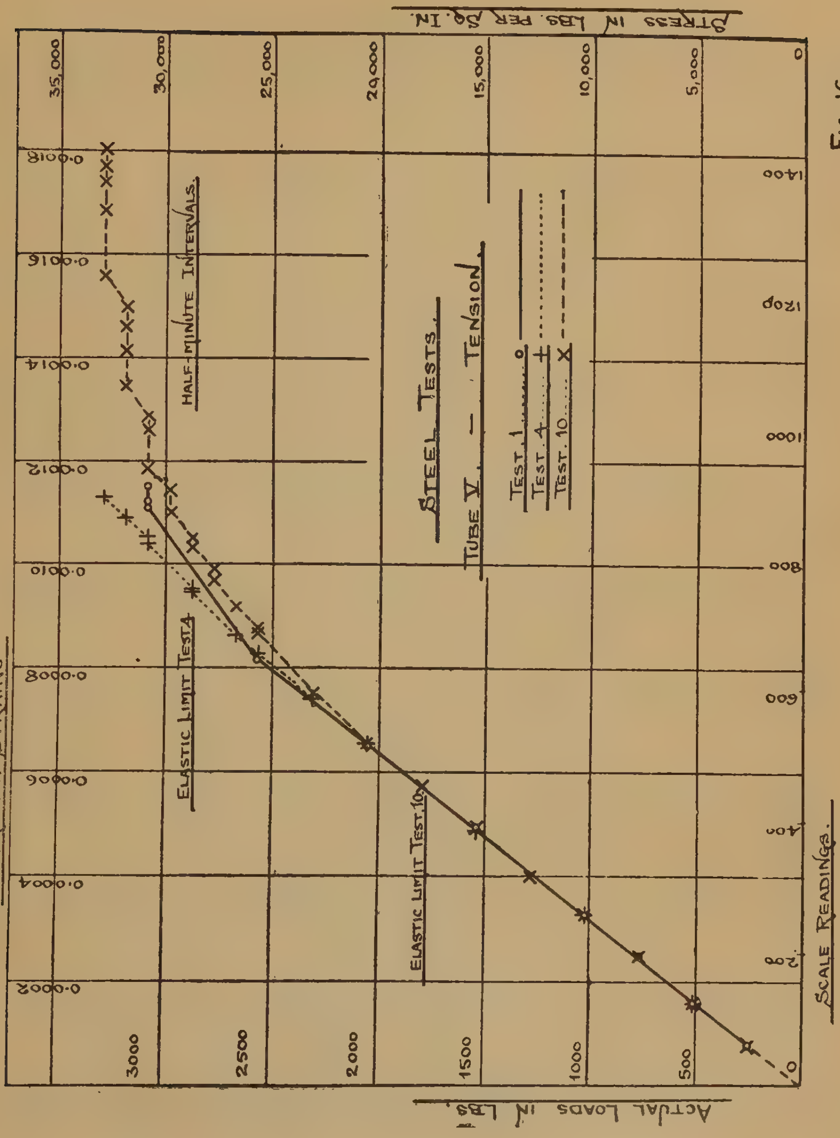


FIG. 16.

Fig. 16.—Tension Tests on Steel.

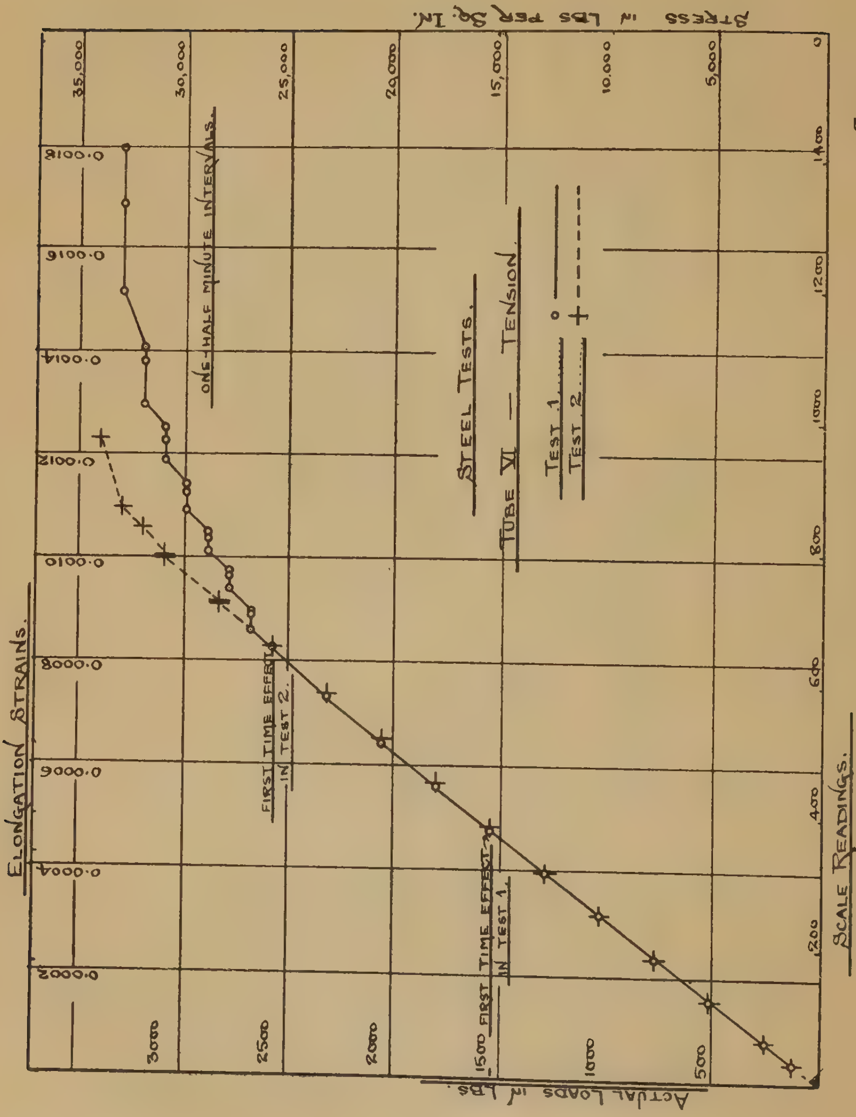


Fig. 17.

Fig. 17.—Tension Tests on Steel.

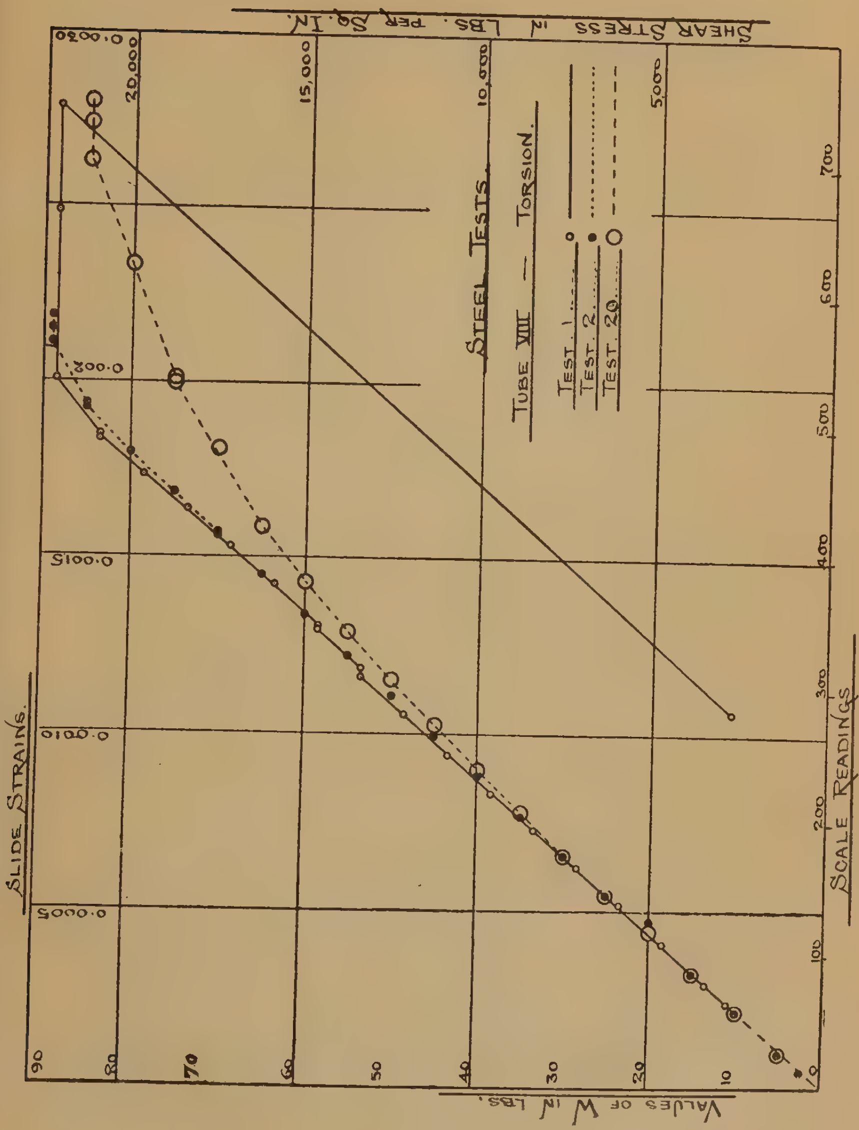


Fig. 18.

Fig. 18.—Torsion Tests on Steel.

by Wöhler in his experiments, is due to gradual increase of size of defects, initially very small; and I think tends to show that the elastic-limit phenomenon is due to the occurrence of the yield-point over small localities.

49. *Yield-point Stresses of same type nearly constant throughout series on each tube.*—It is to be noted that throughout a series of tests on any tube the yield-point stress never having been much exceeded, it has nearly the same value in tests of the same type, though a series of similar tests tend to cause it to rise.

50. *The Variation of the Maximum Stress.*—Proceeding now to a consideration of the variations of the maximum principal stress, of the maximum principal strain, and of the maximum shearing-stress at the yield-points of the different tests, we find that the first-mentioned varies very largely, its least value being found in the pure torsion tests, while in the tests by tension and internal pressure its value is practically constant, and is the same whether the greater of the principal stresses is axial or circumferential. The experiments on Tubes VII. and VIII. show the latter emphatically. We hence conclude, firstly, that in the case of two tensions (such as in a boiler) the lesser tension does not appreciably affect the yield-point; and, secondly, by the similarity of the yield-point stress, whether the greater tension be axial or circumferential, that the material is practically isotropic in respect to the occurrence of the yield-point,—at any rate as regards the tangent-plane stresses, with which we are most concerned.

51. *Variation of the Maximum Principal Strain.*—The maximum strain at the yield-point varies throughout the experiments: it is greatest in the simple tension experiments, and least either in the torsion tests or when the axial and circumferential tensions are equal. Both the strain as measured (where the axial stress is greatest) and as calculated from the stresses and elastic constants (and so not including the elastic-limit effect) are tabulated and can be compared; the calculated maximum strain is sometimes radial and negative. The variations of the maximum strain from constancy are considerable for all the materials experimented upon.

52. *The Maximum Shearing-Stress or Slide nearly constant.*—The maximum shearing-stress developed, and the corresponding maximum shearing-strain or slide (which are quantities directly proportional and independent of the intermediate principal stress within the elastic limit) are comparatively constant, although the amount is highest in the case of pure torsion and diminishes towards the tension case. It will be remembered that the plane of the maximum shear changes from being a tangential plane of the specimen in the torsion-tension cases to a plane intersecting the axis of the specimen in the tension-internal pressure tests.

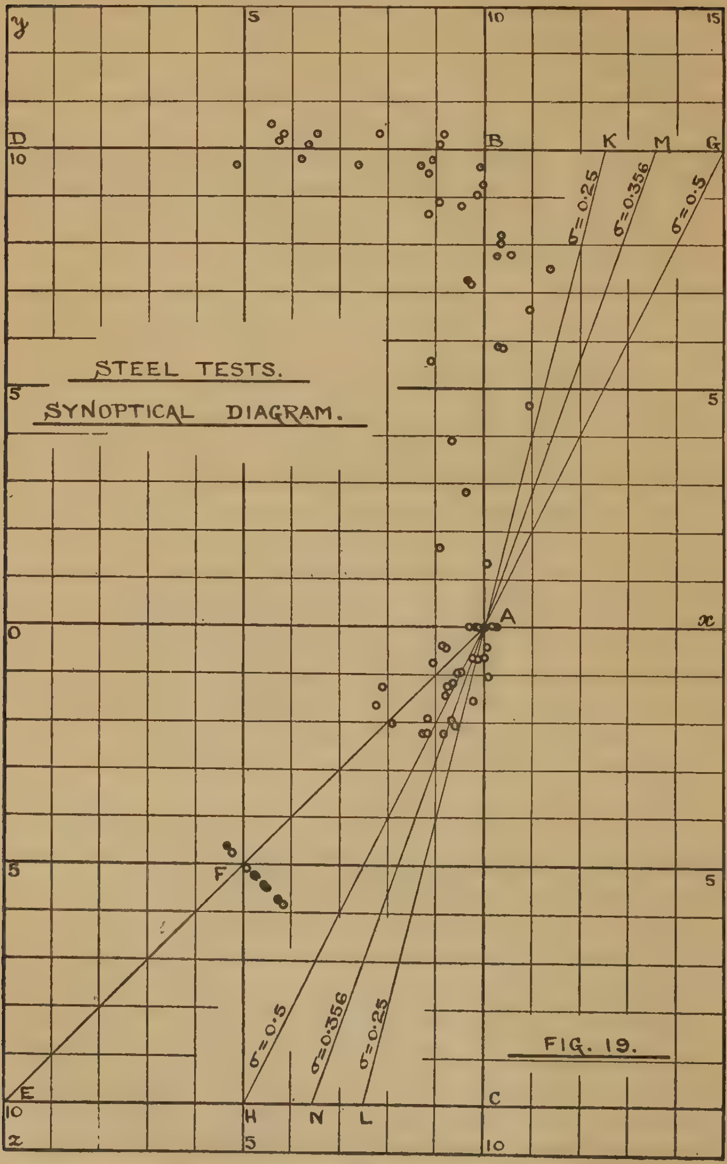
The stresses at the elastic limit have been considered in several cases, and have been found to follow the same variations approximately.

53. *Graphical presentation of Variations.*—The tables and figures may be held to prove, in the case of the materials experimented upon—steel, copper and brass—that to a first approximation the shearing-stress is constant whenever the third principal stress is zero, or whenever the lesser principal stress is zero or small.

It can readily be found by trial that no other simple relation between the stresses or strains is approximately constant.

The results of the series of tests upon steel, with the exception of the unannealed specimens, are shown in fig. 19, which has been constructed as follows :—Ox is the axis of principal stress most nearly coinciding with the generators, and the abscissæ represent the relative values of the stresses in the various experiments, a mean axial yield-point stress being selected as the basis of the scale and marked 10. Relative values of the other principal stresses were then set off parallel to Oy and Oz, those parallel to Oy being the mean, and those parallel to Oz being the minimum principal stress. The paper should be now considered as folded at a right-angle along the line Ox; and the observations recorded in the quadrant $z\,o\,x$ to lie actually on the paper, while those plotted in the quadrant $x\,o\,y$, though nearly in the plane of the paper, should correctly be considered as projected by lines parallel to Oz on to a plane through Ox inclined to the plane $x\,o\,y$ at an angle whose tangent is half the ratio of the internal pressure to the circumferential stress it produces. The value of the

Fig. 19.—Synoptical diagram of Tests.



angle is about $\tan^{-1} 0\cdot0225$, so that the points may be regarded as practically in the plane of the paper.

On the paper are drawn the lines BAC, BD representing the locus of the points had the maximum stress been true; the lines GAH, KAL, MAN, representing the locus had the maximum strain-law been true, and σ had the values 0·5, 0·25, and 0·356 respectively, the latter being the mean experimental value. The constant shearing-stress law locus is the line EFABD, and it will be seen to what extent this agrees with the mean distribution of the observations. No movement of the other lines parallel to themselves can produce any approximation to the mean of the actual distribution.

It must, however, be remembered, while inspecting this figure, that this method of setting out the points was adopted as being just to any theory of strength; had a mean basis been adopted the points could have followed the shearing-stress law much more closely.

54. *Conclusions probable for general type of Stress.*—Considering the three-dimensional view (fig. 20, p. 230), if the shearing-stress law were true the observations plotted in space between Ox, Oy, Oz, or two tensions and a third stress, would fall upon the two planes, EAB, EDB. We have in our experiments investigated such combinations of stresses as give rise to half the line AE, *i. e.* to FA, to AB, and to BD′ which is half BD.

Now a similar figure may be drawn for the strains, and since the traces on the planes $\eta_2=0$ and $\eta_3=0$ in such a figure are straight lines, and since the strains are so small that no quadratic or higher power can have appreciable effect, except in the improbable case of their coefficients being extremely large, the function representing this relation is linear. Since by experiment the value of the intermediate strain has no effect on the yield-point relation, the coefficient of η_2 in the linear relation is zero. The linear relation therefore reduces to the equation of the line AE (or the plane AEB). This line, as determined by experiment, being equally inclined to the axes, the corresponding relation is that the shearing stress or strain is constant.

55. *Effect of a Uniform Volumetric Stress.*—In order to ascertain the relationship of the stresses at the yield-point

more accurately, sequences of tests in which torsion and tension combined in various amounts should be compared, and the inclination of the line AE more accurately determined. From this point of view a direct compression-test would be of much assistance. Now the linear relation may be written

$$\varpi_1 - \varpi_2 + \lambda(\varpi_1 + \varpi_2) = \mathrm{C},$$

since this contains two independent constants. Putting $\varpi_2 = 0$ we get the case of tension only and the yield-point stress from the equation is $\frac{\mathrm{C}}{1+\lambda}$. Putting $\varpi_2 = -\varpi_1$ we get the case of pure torsion, and the yield-point stress is then $\frac{1}{2}\mathrm{C}$. The mean of the experimental results gives for the ratio of these yield-point stresses the value 0·52, for which the value of λ is 0·04; and the relation becomes

$$\varpi_1 - \varpi_2 + 0{\cdot}04(\varpi_1 + \varpi_2) = q_0,$$

where q_0 is the value of the yield-point shearing-stress in pure torsion.

56. *Convenient view of general type of Stress.*—Since the stress ellipsoid $\varpi_1 x^2 + \varpi_2 y^2 + \varpi_3 z^2 = 1$, where $\varpi_1, \varpi_2, \varpi_3$ are in descending order of magnitude, may be written in the form

$$\left(\frac{\varpi_1 + \varpi_2}{2}\right)(x^2 + y^2 + z^2) + \left(\varpi_3 - \frac{\varpi_1 + \varpi_2}{2}\right)z^2 + \frac{\varpi_1 - \varpi_2}{2} xy = 1$$

(since the invariants are the same), it is clear that any state of stress can be represented by the coexistence of a shearing-stress, a volumetric uniform stress, and a stress perpendicular to the plane of the shear; and the yield-point occurs when the shearing-force together with a small fraction of the volumetric stress reaches a certain amount: the volumetric stress being reckoned positive when tensile.

That the coefficient of the volumetric stress for steel is small has been shown by these tests, and that it has some value greater than zero seems probable, as volumetric tension would ultimately reduce the material to the liquid or gaseous form and cause the necessary shear to evanesce. No value can be directly deduced from such considerations owing to lack of knowledge of ultimate molecular action. It may be noted that Bauschinger's experiments on the yield-point in tension and compression, in which the effect of λ would be most marked, would point to zero as its value.

57. *The Copper and Brass Tests, and Diagrams.*—In the case of the copper and brass tests the yield-point is more difficult to locate; the shearing-stress law still appears to be that one of the simple laws nearest to the truth. Taking into account the volumetric stress effect, the coefficient λ is larger than in the case of steel, but so few tests have been made that conclusions should be drawn with hesitation, especially as the yield-point stress tends to rise with the successive tests.

In the copper tests the yield-points were very indefinite, and I have plotted out types of the unusual tests from which the stresses and resulting strains and the mode of their variation can be seen at a glance, and their values at points considered to correspond to the elastic limit or yield-point in the various tests readily compared. These curves are given in figs. 21–24.

In fig. 21 is shown a test under internal pressure only, the stresses parallel to the axis being one-half of the simultaneous circumferential stresses; the values of the internal pressure are laid off along the central line, and the values of the corresponding axial and circumferential strains given on the right and left hand respectively of the figure. The readings of the axial and diametral (fig. 14, p. 230) extensometers are given along the base line, and the corresponding strains along the top of the diagram. The axial strain is laid off positively (extension) towards the right, and the circumferential strain (from the diametral extensometer) positively towards the left.

Fig. 22 represents a combined tension and internal pressure test; the tension load was applied first, the actual loads being marked along the central line and the corresponding stresses along the right-hand side line of the figure. The axial strains are positive and are set off to the right of the central line; the circumferential strains (diametral extensometer) are set off

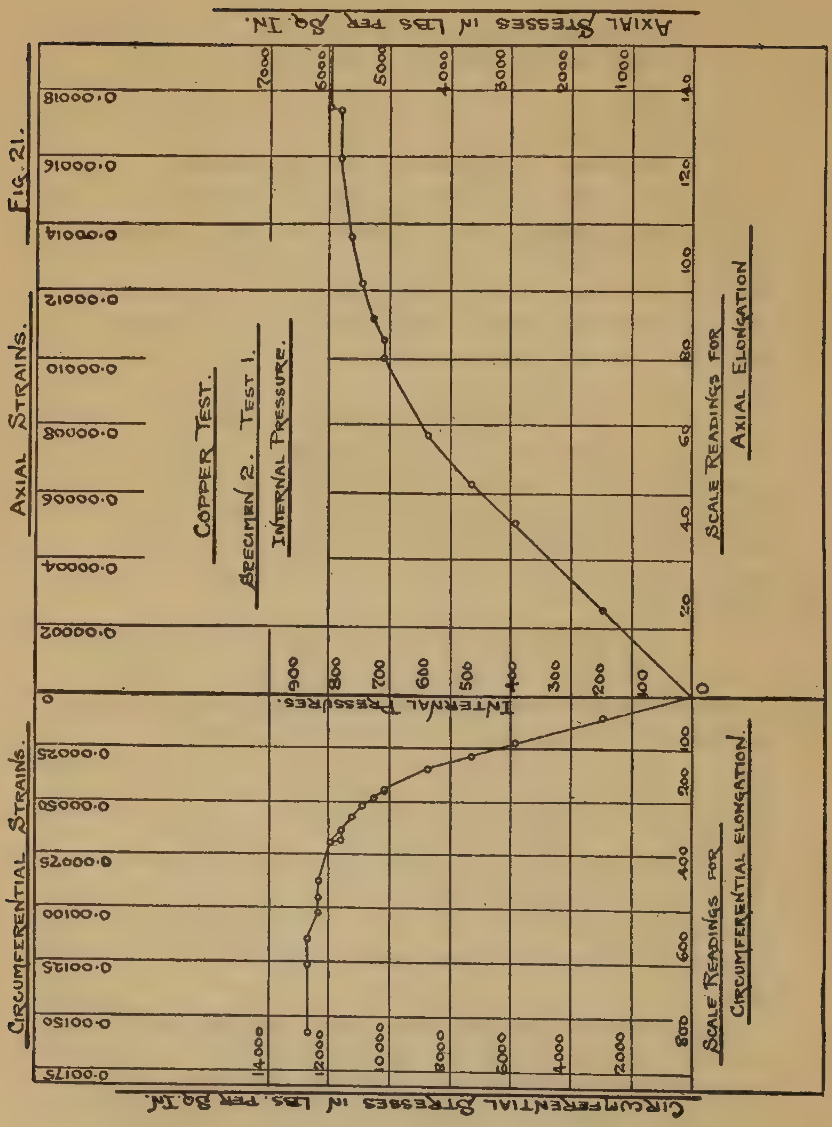


Fig. 21.

Fig. 21.—Copper Test by Internal Pressure.

Fig. 22.

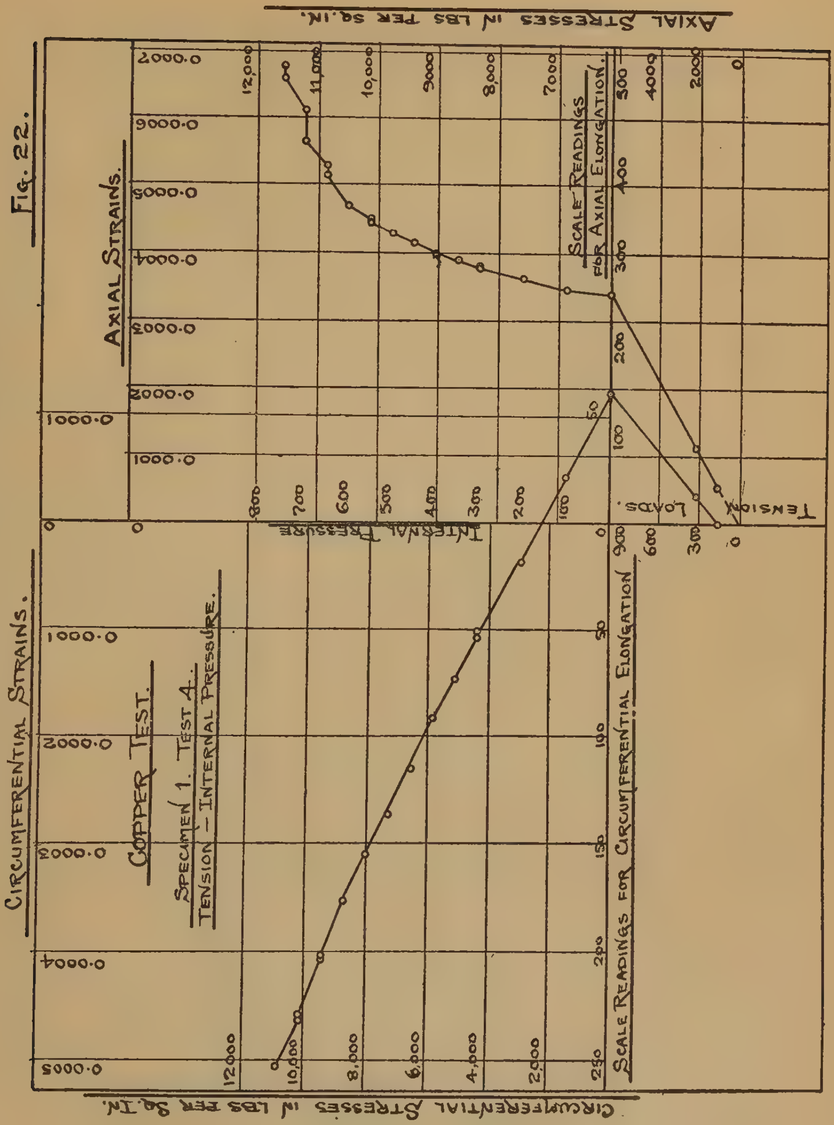


Fig. 22.—Copper Test by Tension and Internal Pressure.

FIG. 23.

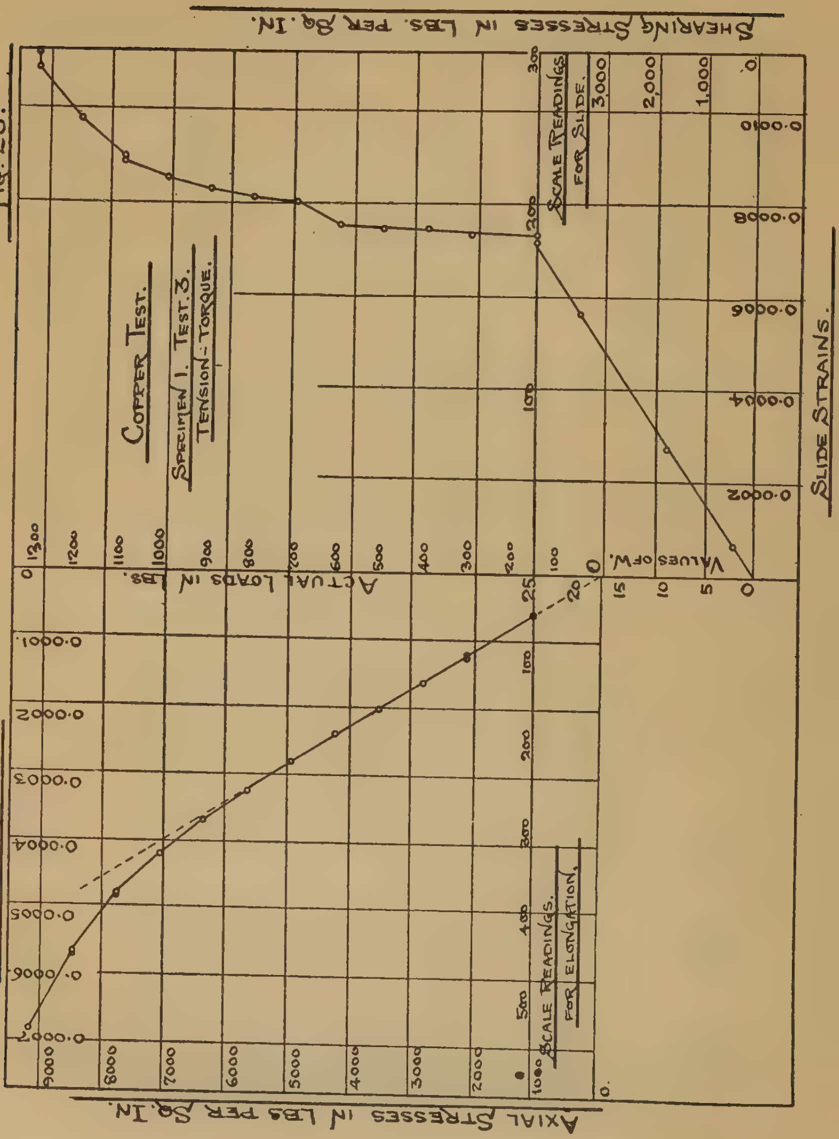


Fig. 23.—Copper Test by Tension and Torque.

Fig. 24.

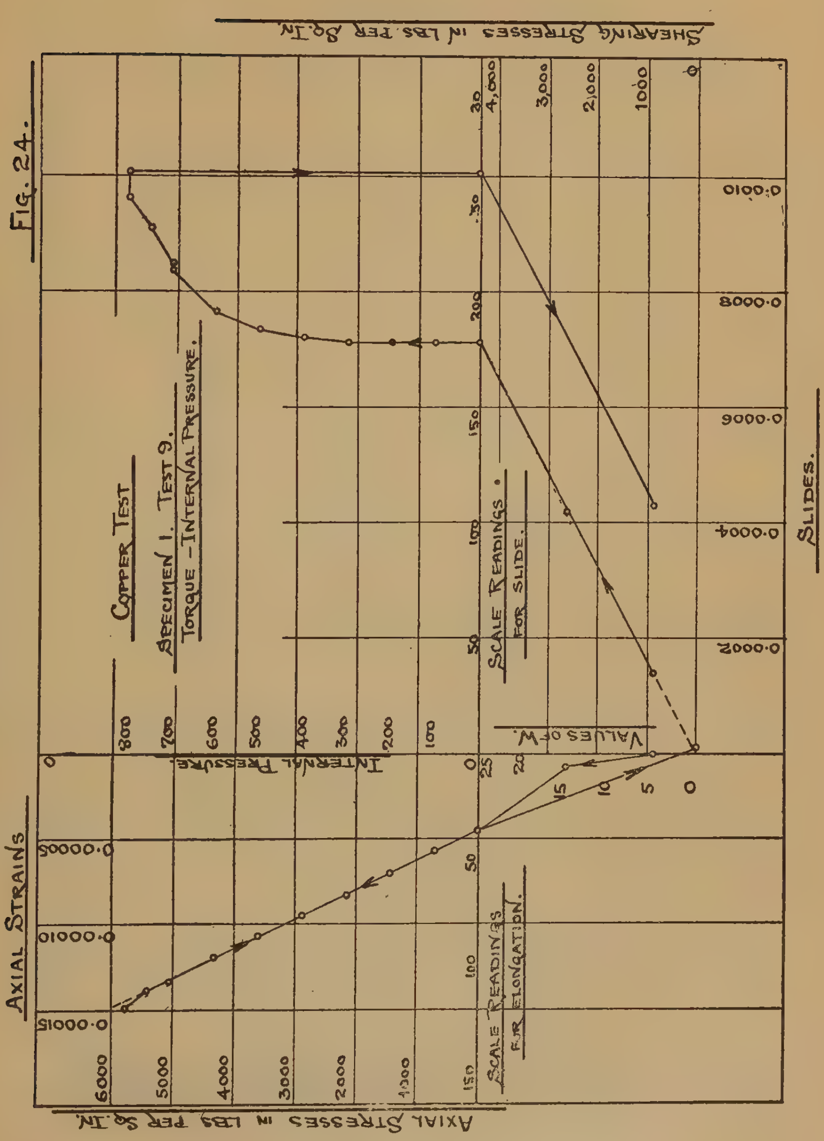


Fig. 24.—Copper Test by Torque and Internal Pressure.

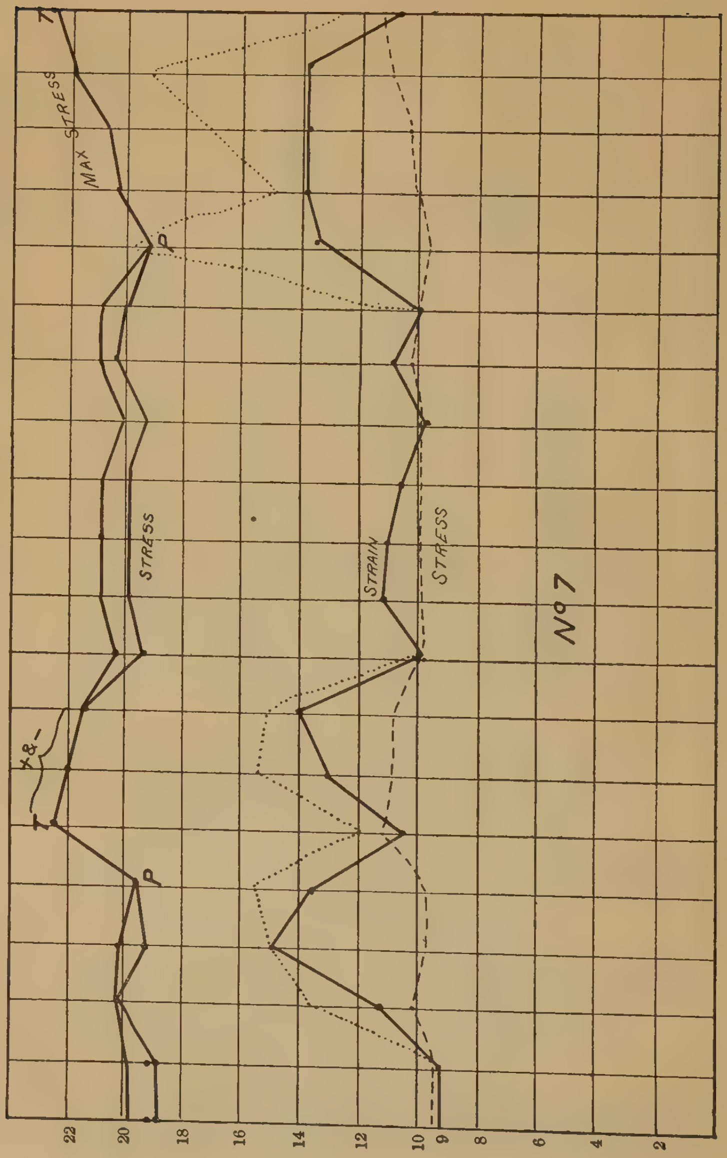
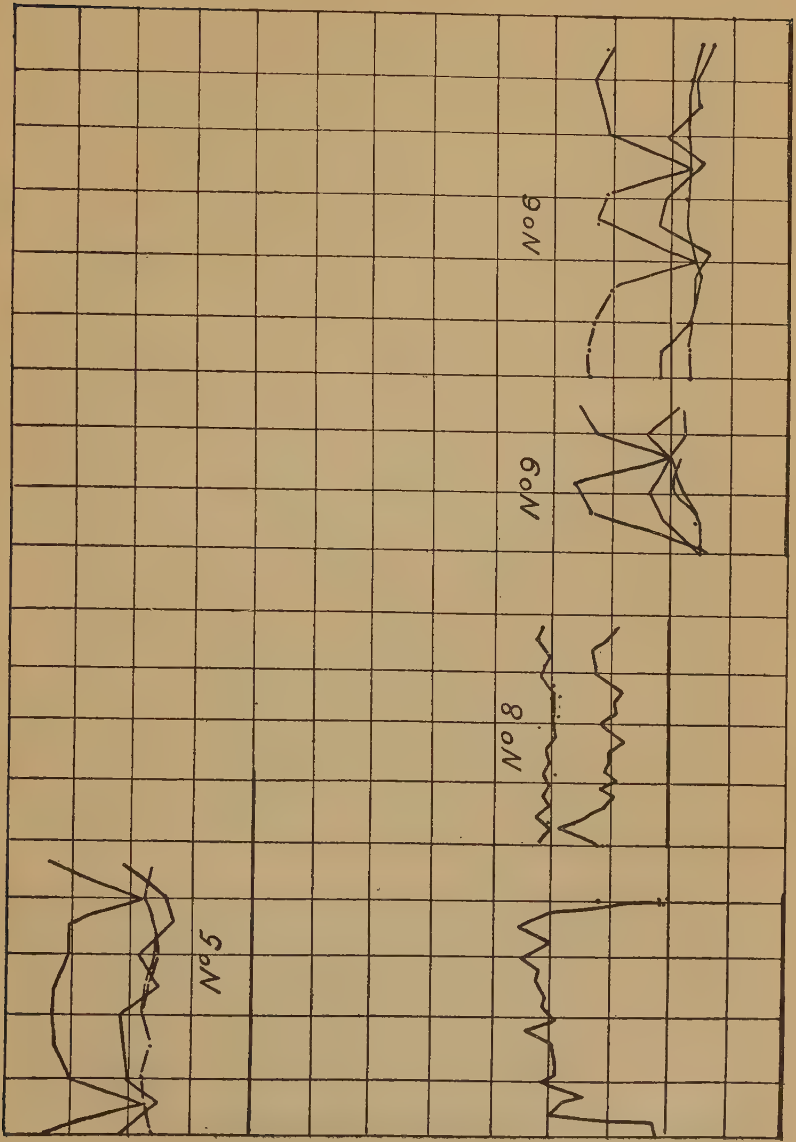


Fig. 25.—Curves showing Variations of Maximum Stress, of Maximum Strain, and Maximum Shear.


No 6
No 9
No 8
No 5

positively to the left of the central line, but during the application of the tension loads this strain is negative, and the stress-strain line therefore bears to the right. After a load of 900 lbs., actual, was reached, the tension load was kept constant and the internal pressure applied; the values are marked off along the central line, the resulting circumferential stresses are given on the left-hand, and the total axial stresses on the right-hand of the diagram. Along the line of no internal pressure are given the actual extensometer readings, the corresponding strains being placed at the top.

Fig. 23 represents a combined tension and torsion test; the torque was applied first, and the values of W are set off along the central line and the corresponding stresses on the right-hand side of the diagram. The shearing-strains or slides are set off to the right of the central line. After W had reached the value of 25 lbs., it was kept constant and the tension-loads applied; it will be noticed that the initial tension-load was 150 lbs. The actual tension loads are recorded along the central line, and the corresponding stresses on the left-hand side; the resulting axial strains are positive to the left of the central line. The principal strains at any point cannot be determined at once from the diagram without a construction or calculation. The addition of a tension load should not change the twist (slide) reading, unless the elastic limit has been passed; the slight inclination of this part of the line may be due to a bending-moment, or to a slight want of isotropy introduced by the previous tests.

Fig. 24 is a similar diagram for a torque and internal-pressure test, and can be readily understood from its similarity to the preceding figures.

All these figures, and the corresponding ones for simple tension and torsion, show the stress-strain line as bending gradually over, the strongly-marked yield-point of iron and steel being absent; they also show how unsatisfactory, in such cases, any tabulation of elastic-limit or yield-point stresses and strains must be. The selection of apparently similar points on the curves, however, leads to the discovery at them of the same amount of shearing-stress.

58. *Practical Conclusions and Note.*—The result, then, of these experiments, as applicable to practice, is that the condition for initial yielding of a uniform ductile material is the existence of a specific shearing-stress; and that the intermediate principal stress is without effect.

Note.—Cases of more than one principal stress are met with most frequently in boilers, hydraulic cylinders, and crank-shafts. In the former cases the results obtained above lead to the same dimensions as are obtained by the consideration of the greatest stress only, while the maximum-strain theory would lead to the adoption of too small a thickness. In the case of crank-shafts, or "combined bending and twisting," both the greatest stress and greatest strain theories lead to too small dimensions, the corresponding well-known formulæ for the "equivalent bending moment" being

$$\tfrac{1}{2}(M+\sqrt{M^2+T^2}) \quad \text{and} \quad \tfrac{3}{8}M+\tfrac{5}{8}\sqrt{M^2+T^2}$$

respectively, where M is the applied bending-moment and T the applied twisting-moment. The greatest shearing-stress theory leads to the (greater) value $\sqrt{M^2+T^2}$ for the equivalent bending-moment, and where the dimensions are thus determined that formula should be used. A lower factor of safety might, however, be used in such cases, where there is a large reserve of understressed material.

It may also be noted that the specific shearing-stress at the yield-point is better determined by taking one half of the tensional yield-point stress, than from the results of torsional experiments in which the sharpness of the yield-point is masked, as explained in § 10 and shown in fig. 15.

[I have pleasure in expressing my thanks for assistance rendered in the tests by Messrs. Ashworth, Howe, Knowles, Rebboli, Nichols, Vail, and Heichert; the latter of whom also assisted me in the construction and erection of the greater part of the apparatus.]

DISCUSSION.

Dr. CHREE (communicated).—Mr. Guest, in his paper, has regarded the shearing-stress theory as a little-known one. As the shearing-stress is half the difference between the greatest and least principal stresses, this theory is the same as the maximum stress-difference theory employed by Prof. G. H. Darwin (following Tresca) in his investigations respecting the state of the earth. He (Dr. Chree) has also employed this theory, as well as the greatest strain theory, in many elastic problems. All the theories presuppose the ordinary mathematical theory of elasticity, which depends on Hooke's law, that the stress-strain relation is linear, and assumes that strains are so small that their squares and products can be neglected. Mr. Guest concludes that, in ordinary materials, the stress-strain relation is linear to the elastic limit, which answers to a stress lower than that which answers to the yield-point, and that yield-point phenomena arise locally before a general yield-point is reached. Nevertheless, he focusses attention on the yield-point as the criterion of strength.

Prof. PERRY congratulated the author upon his paper, and said there was no time left to discuss it at length. The results obtained gave information upon a subject of which very little is known experimentally.

XIX. *Reflexion and Transmission by Condensers of Electric Waves along Wires.* *By* EDWIN H. BARTON, *D.Sc., F.R.S.E., A.M.I.E.E., Senior Lecturer in Physics at University College, Nottingham, and* LOUIS LOWNDS, *B.Sc., 1851 Exhibition Science Research Scholar**.

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INTRODUCTION.

1. IN 1892 J. Ritter von Geitler † experimentally detected the reflexion by a condenser of electric waves along wires. He also examined qualitatively the effects of condensers of various sizes; but no attempt was made to give a complete theory of the various phenomena involved, and by careful quantitative observations compare experiment with theory. This fuller examination one of us, who followed von Geitler under the late Professor Hertz, at Bonn, determined to attempt when opportunity offered. The present paper embodies the result of the work carried out during the session 1898–99 at University College, Nottingham, and advances the problem another stage towards complete solution.

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* Read January 26, 1900.

† "Inaugural Dissertation," Bonn, January 1893. Wied. *Ann.* xlix. pp. 184–195 (1893).

2. The phenomena are more complicated than might be at first supposed. This is chiefly owing to the fact that the wave-train, reflected by the condenser under examination, passes and repasses between the point of reflexion and the oscillator at the beginning of the line. Hence the effect to be observed, owing to reflexion at any condenser, is a function not only of the coefficient of that reflexion but also of the other constants of the circuit. To avoid unnecessary complication, the wave-train transmitted by the condenser is always completely absorbed by a suitable bridge at the end of the line.

3. By placing the electrometer beyond the condenser, the wave-train transmitted is determined, and by placing the condenser *far* beyond the electrometer the wave-train reflected is measured. In order to determine the phase-lag introduced in the reflected wave-train, the condenser is placed in a number of positions, each of which is only a short distance beyond the electrometer. We thus obtain stationary waves by the interference of the incident and reflected wave-trains, and these, explored by the electrometer, exhibit the phase-change sought. To bring this change of phase into clearer relief, stationary waves are also obtained by a resistance-bridge, whose reflexion coefficient is the same as that of the condenser, but whose phase-change is π simply.

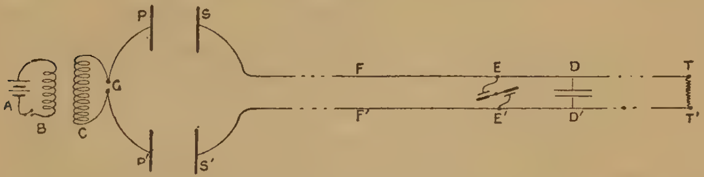
4. The results obtained with the three condensers used are all in fair accord with theory, both as to phase-lag and coefficient of reflexion and transmission. The experimental discrepancy, if such it can be called, is in the direction of less reflected and less transmitted than the long-wave theory predicts.

It may be mentioned here that the experiments, though given in this paper after the theory, were in practice finished before the theory was fully worked out. The experimental results are thus free from any bias due to anticipation based on theory. Each set of readings was accepted simply on the ground of consistency of the separate readings. Further, the experimental curves were in all cases plotted before superposition of the theoretical ones.

Experimental Arrangements.

5. The arrangement of the apparatus adopted for observing the reflected wave-trains is diagrammatically represented in fig. 1. In this figure, A denotes the battery of two storage-cells, B and C are the primary and secondary coils respectively of the induction-coil, of which C has a resistance of 3000 ohms and an inductance of about 20 henries. G is the spark-gap, which was adjusted to 2 mm., the balls being of brass, highly polished before each occasion of experimenting. The wire PGP′, measured along the semicircle, is about 2 metres long. PP′ are the edge-views of the condenser-plates of zinc 40 cm. diameter placed opposite to and 30 cm. distant from the precisely similar disks S S′.

Fig. 1.—Circuit arranged for Reflected System and for Interference Phenomena.



6. The line is represented by SEDTT′D′E′S′, and consists of two parallel copper wires, 1·5 mm. diam., and kept 8 cm. apart by wood separators at intervals of about 1 metre. These wood separators are about 12 cm. long, 2·5 cm. wide, and 1·2 cm. thick, and were well saturated before use in melting paraffin-wax. Their resistance was thus raised to something over 60,000 megohms each, which thus renders the leakage of the line quite negligible.

7. EE′ denotes the electrometer, which has a single plane needle initially uncharged, and suspended by a fine quartz fibre between two disks attached to the line at E and E′. The needle is therefore electrified by induction whenever a wave-train passes EE′, and its ends are consequently attracted to the disks whatever the sign of their potential-difference. The first throw of the electrometer is thus proportional to the time-integral of the square of the potential-difference. The needle is provided with weak magnetic control and a plane mirror by Adam Hilger, its indications being read by

a distant telescope and scale. The induction-coil is put on end to avoid any magnetic effect on the electrometer-needle. The leads also of the coil are kept close together, and, before taking a set of readings, the electrometer is tested as to the adequacy of these precautions against possible disturbance. The disks and the ends of the needle are each about 2 cm. diam. and 1 cm. apart. It will be shown later that the reflexion of waves at the electrometer, regarded as a condenser on the line, is extremely small and quite negligible.

8. TT′ denotes the terminal bridge which is used to absorb the waves on arrival at the end of the line. It consists of graphite markings on a disk of ground glass, 3 inches diameter, and before each set of readings is adjusted to the resistance which corresponds to complete absorption; namely, for the line in question, 560 ohms *.

DD′ denotes one of the condensers in use to reflect the waves. For the transmitted system they are removed from DD′ and inserted at FF′. They were all three made of disks of zinc 1 cm. apart, their radii being respectively 15, 9, and 5 cm. The two disks were kept at the right distance apart, and insulated by pieces of wood saturated in paraffin-wax, notched and secured with shellac.

9. The total length of the line from S to T is of the order 166 metres. The distance SE is 116 metres, SF is of the order 60 metres. ED varies from about ·75 metre to 50 metres. Exact details will be given in connexion with the various experiments.

10. The waves generated by the primary oscillator are of the damped simple harmonic type 8·5 metres long, their logarithmic decrement per wave being 0·6. Thus the wave-train launched upon and propagated along the line with the speed of light is a damped train with its large end or head leading, the tail, after about 10 or 12 waves, being almost negligible. As the waves proceed along the line they suffer attenuation, also some loss on reflexion at the oscillator. The constants expressing these effects were previously determined experimentally on the line now in use, and their numerical values will be introduced into the theory later.

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* "Absorption of Electric Waves, &c.," Phil. Mag., January 1897.

THEORY.

11. *Preliminary.*—The plan adopted throughout the experiments is to take (1) readings of the electrometer with no condenser on the line, but only the absorbing-bridge at the end; alternated with (2) electrometer-readings with a condenser on the line at an intermediate position, as well as the absorbing-bridge at the end. The mean ratio of the readings under the different conditions constitutes the experimental estimate of the effect produced by the condenser in question when in that position.

12. In order, however, to interpret the experimental results and compare them with theory, we need to trace the history of the wave-train reflected by the condenser until it is, practically, extinguished by its losses through repeated reflexion and attenuation. The effect at the electrometer when no condenser is on the line may be represented by a single time-integral which, without sensible error, owing to the damping of the wave-train, may be taken from the commencement of the time to infinity. The effect at the electrometer when a condenser is on the line requires, however, an infinite series of integrals.

13. To construct this series we must first determine the various elements of which it consists. We must accordingly treat the case of a condenser on the line, *not* at the end. This will be referred to as an *intermediate* condenser. We have here to determine the coefficients of reflexion and transmission and the phase-lags of both the reflected and transmitted portions. The case of a *terminal* condenser must also be treated, since the oscillator at the beginning of the line falls under this category. Here, only two constants are required, the amplitude and phase of the reflected portion. These points will now be dealt with in order, together with subsidiary matters that crop up by the way and are included for the sake of completeness.

14. We shall treat the circuit throughout as what Mr. Oliver Heaviside terms a "distortionless circuit," not that it is strictly distortionless, but because it is very nearly so; and this treatment, while sacrificing nothing of material accuracy,

considerably simplifies the analysis. Prof. W. B. Morton* has shown that for the circuit in question the errors thus involved are less than one in a thousand.

15. *Intermediate Condenser.*—At the place of attachment of the condenser let ϕ_1 denote the potential-difference of the two wires of the line due to the arrival there of the incident wave-train. Then ϕ_1 is a function of the time. Similarly let ϕ' and ϕ_2 correspond to the reflected and transmitted wave-trains respectively. Then by consideration of potential and Heaviside's theory of the distortionless circuit, assumed valid to the head of the wave-trains, we have

$$\left.\begin{aligned} &\phi_1+\phi'=\phi_2=\mathrm{Q/S'}, \\ &i_1=\phi_1/\mathrm{L}v,\ i'=-\phi'/\mathrm{L}v,\ i_2=\phi_2/\mathrm{L}v, \\ &i_1+i'-i_2=\frac{d\mathrm{Q}}{dt}, \\ &\mathrm{Q}=\phi_2=0 \text{ for } t=0; \end{aligned}\right\} \quad . \quad . \quad . \quad (1)$$

where Q is the quantity of electricity at time t on the positively charged plate of the condenser of capacity S′ (in electromagnetic units), and the i's denote the currents in the positive wires due to the wave-trains denoted by the ϕ's bearing the same subscript or dash; L denotes the inductance of the line per unit-length, and v is the speed of free æther radiation. These equations were used by Heaviside with reference primarily to waves of telephonic frequency, but are here adopted as a working approximation for the phenomena which obtain in the case of Hertzian waves.

On eliminating the i's and Q, we have

$$\left(\mathrm{L}v\mathrm{S}'\frac{\partial}{\partial t}+2\right)\phi'=-\mathrm{L}v\mathrm{S}'\frac{\partial}{\partial t}\phi_1, \quad . \quad . \quad . \quad (2)$$

and

$$\left(\mathrm{L}v\mathrm{S}'\frac{\partial}{\partial t}+2\right)\phi_2=2\phi_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These expressions might have been written at once from Heaviside's operational results, the reflexion and transmission coefficients for an intermediate bridge being respectively

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* Phil. Mag., March 1899; Proc. Phys. Soc. vol. xvi. p. 281.

$$\frac{-\mathrm{L}v}{2\mathrm{Z}+\mathrm{L}v} \text{ and } \frac{2\mathrm{Z}}{2\mathrm{Z}+\mathrm{L}v}, \quad . \quad . \quad . \quad . \quad (4)$$

where the resistance operator Z is here equivalent to

$$\left(\mathrm{S}'\frac{\partial}{\partial t}\right)^{-1}$$

since the bridge is a condenser merely.

16. Now if the incident wave-train is a damped sine function right up to its head, we may write without loss of generality,

$$\phi_1 = e^{-kpt}\cos(pt+\iota). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Substituting this value of ϕ_1 in equations (2) and (3), and satisfying the initial conditions expressed in (1), we obtain in the usual way the following solutions :—

$$\phi' = \mathrm{A}e^{-kpt}\cos(pt+\iota+\alpha) - \mathrm{B}\cos(\iota+\beta)e^{-2pt/\chi'}, \quad . \quad (6)$$

$$\phi_2 = \mathrm{B}e^{-kpt}\cos(pt+\iota+\beta) - \mathrm{B}\cos(\iota+\beta)e^{-2pt/\chi'}; \quad . \quad (7)$$

where

$$\left.\begin{array}{ll} \mathrm{A}\cos\alpha = \dfrac{-\chi'^2+2k\chi'-k^2\chi'^2}{\Delta'} & = a, \\ \mathrm{A}\sin\alpha = -2\chi'/\Delta' & = a', \\ \mathrm{B}\cos\beta = \dfrac{4-2k\chi'}{\Delta'} = b = & 1+a, \\ \mathrm{B}\sin\beta = -2\chi'/\Delta' = b' = & a', \\ \quad \Delta' = 4+\chi'^2-4k\chi'+k^2\chi'^2, & \\ \text{and} & \\ \quad \chi = \mathrm{L}v\mathrm{S}'p. & \end{array}\right\} \quad . \quad . \quad (8)$$

We have then finally

$$\left.\begin{array}{l} \mathrm{A} = +\sqrt{a^2+a'^2}, \qquad \tan\alpha = a'/a, \\ \mathrm{B} = +\sqrt{b^2+b'^2} \text{ and } \tan\beta = b'/b. \end{array}\right\} \quad . \quad . \quad (9)$$

The algebraic signs of a, a', b, and b' being preserved show in which quadrants α and β should be taken.

17. We see from (6) and (7) that the reflected and transmitted wave-trains consist each of a damped periodic part and a purely exponential part. The exponential part we shall

have to omit from the first portion of the subsequent analysis, because we have no experimental proof of the exact shape of the head of the incident wave-train. For the same reason we shall at first omit the ι also. The greatest correction which this approximate theory can in any possible case require will be subsequently discussed and evaluated. (See arts. 60 and 61.)

18. Under these simplifications we may compactly represent the three wave-trains as follows :—

$$\left.\begin{array}{l}\text{Incident wave-train, real part of } \epsilon^{(i-k)pt},\\ \text{Reflected wave-train, real part of } (a+a'i)\epsilon^{(i-k)pt},\\ \text{Transmitted wave-train, real part of } (b+b'i)\epsilon^{(i-k)pt};\end{array}\right\} \quad (10)$$

where a, a', b and b' have the values assigned to them in (8) and have been confirmed by Heaviside's operational methods.

19. It may be noted in passing that if the incident wave-train were not damped, the reflected and transmitted trains would differ in phase by $\frac{\pi}{2}$ exactly. For on putting $k=0$ in the expressions for $\tan\alpha$ and $\tan\beta$ they become $\frac{-2}{-\chi'}$, and $\frac{-\chi'}{2}$ respectively, hence their product is -1. This simple relation is seen to be slightly modified by the damping.

Again, if the damping were not present, we should have the simple result $A^2+B^2=1$, as should be the case, showing that the sum of the energies of the reflected and transmitted wave-trains equals the energy of the incident one. To effect the corresponding check for the damped waves, one would need to take the time-integrals from zero to infinity of the square of the amplitude for the incident, reflected, and transmitted wave-trains, the exponential terms being no longer ignored.

As a further check it may be noted that the equation for potential-difference at the condenser is always satisfied. For the equation in question, viz.: $\phi_1+\phi'=\phi_2$, reduces to $1+a=b$ and $b'=a'$, and by (8) this is an identity for all values of k and χ'.

20. If the capacity of the condenser be imagined to increase from zero to infinity, while the circuit and the incident wave-train are maintained the same, we see by equations (6) and (8) that the reflexion-coefficient A grows from zero to unity, while the phase-difference α, but for the slight modification due to damping, changes from $\frac{-\pi}{2}$ to $-\pi$. Similarly, a reference to equations (7) and (8) shows that as the capacity of the condenser changes from zero to infinity the transmission-coefficient B changes from unity to zero, while the phase-difference, but for the damping, changes from zero to $\frac{-\pi}{2}$.

21. These features for several sizes of condenser are exhibited in Table I., and are graphically represented in figs. 2, 3, and 4, in which the dotted lines represent the values which the coefficients would assume if there were no damping, and the full lines the corresponding values for the damping actually present in the experimental case in question. The incident, reflected, and transmitted amplitudes are shown by OI, OR, and OT respectively. The curves in fig. 5 show at one glance the continuous changes in A, α, B, and β as the

Fig. 2.—Reflexion and Transmission at Small Condenser.

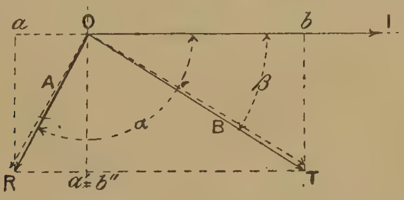


Fig. 3.—Reflexion and Transmission at Medium Condenser.

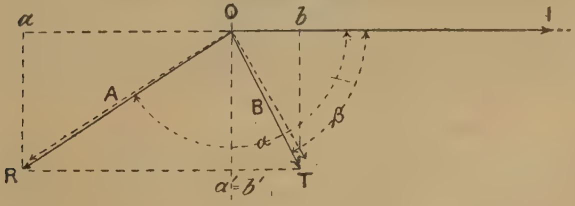


Fig. 4.—Reflexion and Transmission at Large Condenser.

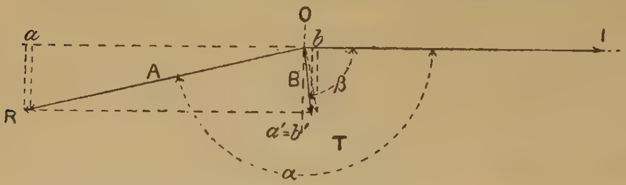
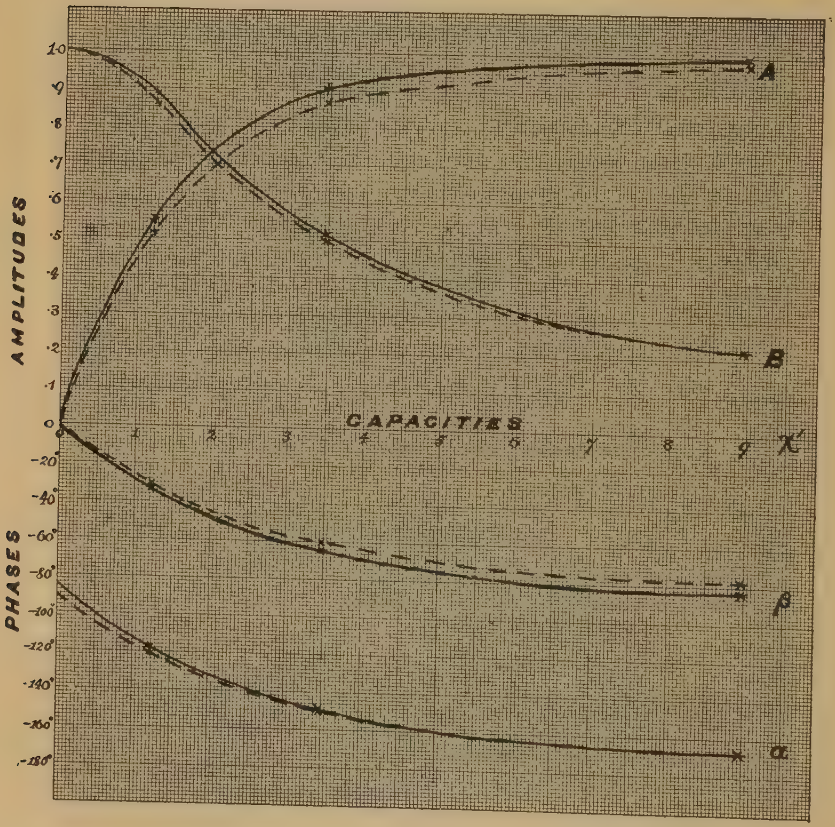


Fig. 5.—Amplitudes and Phase Changes of Reflected and Transmitted Waves with Damping and without.



capacity changes without break from zero towards infinity. Here, again, the full lines show the values of the constants for the damping actually in use, and the broken lines the ideal values when damping is absent.

Table I.—Reflexion and Transmission Constants of Intermediate Condensers.

Condenser Constant $\chi' = LvS'p$.	Constants of Reflected Wave-Train.				Constants of Transmitted Wave-Train.				Damping Constant of Incident Wave-Train.
	a.	*a'*.	A.	*α*.	*b*.	*b'*.	B.	*β*.	
0	0	0	0	$-\frac{\pi}{2}$	+1	0	+1	0	Zero, *i. e.* Incident Wave-Train Undamped.
1·21	−·268	−·443	+·518	−121° 10′	+·732	−·443	+·856	−31° 10′	
3·47	−·751	−·433	+·867	−150° 5′	+·249	−·433	+·500	−60° 5′	
8·95	−·952	−·214	+·976	−167° 25′	+·048	−·214	+·22	−77° 25′	
∞	−1	0	+1	$-\pi$	0	0	0	$-\frac{\pi}{2}$	
0	0	0	0	− 84° 36′	+1	0	+1	0	Incident Wave-Train is $e^{-kpt}\cos pt$ where $k=0·0955$ as in Experimental Case.
1·21	−·249	−·483	+·543	−117° 16′	+·751	−·483	+·89	−32° 46′	
3·47	−·775	−·468	+·906	−148° 52′	+·225	−·468	+·52	−64° 19′	
8·95	−·972	−·220	+·994	−167° 16′	+·028	−·220	+·22	−82° 43′	
∞	−1	0	+1	$-\pi$	0	0	0	−95° 24′	

22. *Reflexion at Electrometer negligible.*—It is now necessary to inquire whether the electrometer reflects any appreciable part of the wave-train incident upon it. As previously mentioned, this is not the case.

Between the disks attached to the line at EE′ (fig. 1) the ends of the needle are interposed, each disk with its adjacent needle-end forming a condenser whose plates are 1 centim. radius and 1 centim. apart. The electrometer as a whole constitutes a set of two such condensers in series. Hence the capacity interposed between E and E′ is half that due to one disk and needle-end.

Taking the correction for the edges of the plates in a parallel disk condenser given in Kohlrausch's 'Practical Physics,' we thus obtain S′, the capacity between E and E′, equals $\frac{1}{3} \times 10^{-21}$ in electromagnetic c.g.s. units. And for the present experimental case, $Lv = 56 \times 10^{10}$ and $p = 2 \times 10^{8}$ in the same units. Hence $\chi'=\mathrm{L}v\mathrm{S}'p=\cdot037$, $a=-\cdot00035$, $a'=-\cdot019$, and $\mathrm{A}^2=a^2+a'^2=\cdot00036$.

Thus the energy reflected by the electrometer is of the order 0·04 per cent. of that incident upon it, and is therefore quite negligible.

23. *Intermediate Resistance.*—It seems desirable for the purpose of contrast with the reflexion from a condenser to consider now that of an intermediate resistance. In this case the phase-change introduced does not vary with the amplitude coefficient. But, however the resistance is varied, the phase-change introduced in the reflected wave-train remains constant and equal to a lag of π.

24. Thus, using the same notation as before, we have the following equations as the conditions connecting potential-difference and current where a bridge of resistance R′ is placed on the line, the line being understood to extend beyond it.

$$\phi_1+\phi'=\phi_2,$$

$$i_1=\phi_1/\mathrm{L}v,$$

$$i'=-\phi'/\mathrm{L}v.$$

$$i_2=\phi_2/\mathrm{L}v,$$

$$i_1+i'-i_2=\phi_2/\mathrm{R}'.$$

Whence, on elimination of the i's, we obtain

$$\frac{\phi'}{\phi_1}=\frac{-\mathrm{L}v}{2\mathrm{R}'+\mathrm{L}v} \quad \text{and} \quad \frac{\phi_2}{\phi_1}=\frac{2\mathrm{R}'}{2\mathrm{R}'+\mathrm{L}v}.$$

25. Or, we may say that if the incident wave-train be a cosine function of the time, damped or not, the reflexion-coefficient and phase-change are respectively

$$\mathrm{A}'=\frac{+\mathrm{L}v}{2\mathrm{R}'+\mathrm{L}v}, \quad \text{and} \quad \alpha'=-\pi. \quad . \quad . \quad (11)$$

Similarly, the amplitude-coefficient and phase-change for the transmitted wave-train are seen to be respectively

$$\mathrm{B}'=\frac{+2\mathrm{R}'}{2\mathrm{R}'+\mathrm{L}v}, \quad \text{and} \quad \beta'=0. \quad . \quad . \quad . \quad (12)$$

26. *Terminal Condenser.*—Let the capacity of the condenser at the end of the line be S_0, the previous notation for

incident and reflected waves &c. being retained. We then have

$$\left.\begin{aligned} \phi_1+\phi' &= \mathrm{Q}/\mathrm{S}_0, \\ i_1=\phi_1/\mathrm{L}v, \quad i' &= -\phi'/\mathrm{L}v, \\ i_1+i' &= \frac{\partial \mathrm{Q}}{\partial t}, \\ \mathrm{Q}=\phi_1+\phi' &= 0, \quad \text{for } t=0. \end{aligned}\right\} \quad . \quad . \quad (13)$$

On elimination of Q and the i's these equations yield

$$\left(1+\mathrm{L}v\mathrm{S}_0\frac{\partial}{\partial t}\right)\phi' = \left(1-\mathrm{L}v\mathrm{S}_0\frac{\partial}{\partial t}\right)\phi_1 ; \quad . \quad . \quad (14)$$

which is equivalent to Heaviside's expression for reflexion at a terminal condenser.

27. Writing for the incident wave-train

$$\phi_1 = e^{-kpt}\cos(pt+\iota),$$

the solution of (14) may be written

$$\left.\begin{aligned} &\phi' = \mathrm{C}e^{-kpt}\cos(pt+\iota+\gamma) - (\cos i + \mathrm{C}\cos \iota+\gamma)e^{-pt/\chi_0}; \\ &\text{where} \qquad \mathrm{C}\cos\gamma = \frac{1-\chi_0^2-k^2\chi_0^2}{\Delta_0} = c, \\ &\qquad\qquad \mathrm{C}\sin\gamma = \frac{-2\chi_0}{\Delta_0} = c', \\ &\qquad\qquad \mathrm{C} = +\sqrt{c^2+c'^2}, \\ &\qquad\qquad \tan\gamma = \frac{c'}{c} = \frac{-2\chi_0}{1-\chi_0^2-k^2\chi_0^2}, \\ &\chi_0 = \mathrm{L}v\mathrm{S}_0 p, \quad \text{and} \quad \Delta_0 = 1+\chi_0^2-2k\chi_0+k^2\chi_0^2. \end{aligned}\right\} (15)$$

Or, if we ignore, as before, the exponential term and let the incident wave-train be the real part of $e^{(i-k)pt}$, then the solution is

$$\phi' = (c+c'i)\phi_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

the c's having the values given in equations (15).

In the case of a terminal condenser we see that if $k=0$, $\mathrm{C}=1$ for all values of χ_0. This simple relation is slightly disturbed by the damping when present.

28. This theory of the terminal condenser has been given for the sake of dealing with the reflexion which occurs at the

oscillator at the beginning of the line. It may be approximately treated as a condenser simply, because the interval elapsing between the launching of the wave-train along the line and its return after traversing about 300 metres is so small (say one-millionth of a second), that we may regard the spark-gap of the primary as hot enough to act as a short circuit to the secondary of the induction-coil, whose inductance is of the order 20 henries.

29. *Electrometer-throw for Single Passage of Wave-train.*—It might at first be supposed that the phase at the head of a wave-train would have no effect on the electrometer-throw, except when that wave-train was interfering with another, and so producing stationary waves in the neighbourhood of the electrometer. This, however, is not the case. On the contrary, the throw produced by the passage of a single wave-train of given amplitude, period, and damping depends to some extent on the initial phase. Thus we have

$$\int_0^\infty [e^{-kpt}\cos(pt+\iota)]^2 dt = \frac{1-k\sin 2\iota+k^2(1+\cos 2\iota)}{4kp(1+k^2)} . \quad (17)$$

Hence, although we have hitherto been compelled, in one or two cases, to sacrifice rigour on minor points on account of insufficient data, the initial phase of a wave-train will hereafter always be taken account of when dealing with reflexions for which theory furnishes the value of the phase-change to be expected.

It may be seen from (17) that where $k=0{\cdot}1$ the value of the integral varies with ι between limits having the ratio 11 to 9 approximately.

30. *Transmitted System.*—Let the condenser under examination be at a point on the line distant l cm. from its beginning at the oscillator, and let the electrometer be l_2 cm. beyond the condenser, *i. e.* $l+l_2$ from the beginning of the line. Take the origin of coordinates at the condenser, and let the potential-difference of the wires due to the incident wave-train be represented by ϕ_1, where

$$\phi_1 = e^{-kp(t-x/v)-\sigma x}\cos p(t-x/v). \quad . \quad . \quad (18)$$

The σ here provides for the attenuation of the waves in their passage along the line. Its value has been previously determined experimentally.

The train incident at the condenser is accordingly

$$\phi_1 = e^{-kpt}\cos pt. \quad \ldots\ldots \quad (19)$$

31. Now, owing to the irregularity of the sparks at the primary oscillator, it is necessary in the experimental examination of any condenser to alternate electrometer-readings with and without the condenser on the line; the bridge which absorbs all waves incident upon it being throughout in place at the end of the line.

We have therefore to determine theoretically the ratio y, of the mean reading d' with the condenser on the line, to the mean reading d with no condenser on. Now the electrometer-throw, as previously explained, is proportional to the time-integral of the square of the amplitude of the wave-train passing it. Hence, denoting by E the electrometer-constant, we have

$$\mathrm{E}d = e^{-2\sigma l_2}\int_{l_2/v}^{\infty} e^{-2kp(t-l_2/v)}\cos^2 p(t-l_2/v)\,dt$$

$$= e^{-2\sigma l_2}\int_{0}^{\infty} e^{-2kpt}\cos^2 pt\,dt,$$

or

$$4kp(1+k^2)\,e^{2\sigma l_2}\mathrm{E}d = 1+2k^2. \quad \ldots \quad (20)$$

32. Consider now the throw d' obtained with the condenser on the line. Retaining the previous notation for the transmission and reflexion operators of the condensers we have for the wave-trains successively transmitted at the condenser the following series:—

$$\left.\begin{array}{lll} \text{First wave-train:} & & \mathrm{B}e^{-kpt}\cos(pt+\beta), \\ \text{Second} & \text{do.} & \mathrm{CAB}e^{-kpt-2l\sigma}\cos(pt+\gamma+\alpha+\beta), \\ \text{Third} & \text{do.} & \mathrm{C^2A^2B}e^{-kpt-4l\sigma}\cos(pt+2\gamma+2\alpha+\beta). \\ & & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{array}\right\} \quad (21)$$

The formation of this series is easily traced by noting that each time a wave-train is incident upon the condenser, not only is a part transmitted but also a part is reflected, suffers attenuation along the line in its passage to the oscillator, is there reflected, and again suffers attenuation along the line before reaching the condenser a second time. These effects are all provided for in the above series, in which also the simplification is adopted of taking $t=0$ for each new arrival of a wave-train at the condenser.

33. We thus have, on taking the time-integrals of the squares of the successive trains, the following series:—

$$\begin{aligned} \mathrm{E}d'e^{2\sigma l_2} &= \mathrm{B}^2\int_0^\infty e^{-2kpt}\cos^2(pt+\beta)dt \\ &+r^2\mathrm{B}^2\int_0^\infty e^{-2kpt}\cos^2(pt+\beta+\kappa)dt \\ &+r^4\mathrm{B}^2\int_0^\infty e^{-2kpt}\cos^2(pt+\beta+2\kappa)dt \\ &+\ldots\ldots + \ldots\ldots + \ldots\ldots, \quad . \quad . \quad . \quad (22) \end{aligned}$$

where $r=\mathrm{CA}e^{-2l\sigma}$ and $\kappa=\alpha+\gamma$.

Now all the above integrals fall under the type

$$\int_0^\infty e^{-2kpt}\cos^2(pt+\delta)\,dt=\frac{1-k\sin 2\delta+k^2(1+\cos 2\delta)}{4kp(1+k^2)}. \quad (23)$$

Further, the series, to which (22) when integrated gives rise, are represented by

$$\begin{aligned} &\sin\phi+r^2\sin\overline{\phi+\psi}+r^4\sin\overline{\phi+2\psi}+\ldots\ldots \\ &\qquad=\frac{\sin\phi-r^2\sin\overline{\phi-\psi}}{1-2r^2\cos\psi+r^4}. \quad . \quad . \quad . \quad . \quad (24) \end{aligned}$$

Hence (22) is easily transformed to

$$\begin{aligned} &4kp(1+k^2)\mathrm{E}d'e^{2\sigma l_2} \\ &=\mathrm{B}^2\left\{\frac{1}{1-r^2}-\frac{k}{\mathrm{D}}(\sin 2\beta-r^2\sin\overline{2\beta-2\kappa}) \right. \\ &\left. \qquad+\frac{k^2}{1-r^2}+\frac{k^2}{\mathrm{D}}(\cos 2\beta-r^2\cos\overline{2\beta-2\kappa})\right\}; \quad . \quad (25) \end{aligned}$$

where $\mathrm{D}=1-2r^2\cos 2\kappa+r^4$.

34. Now in the experimental case under consideration k is less than 0·1; we may therefore, for the order of accuracy aimed at, simplify by neglect of k^2. Then dividing (25) by

(20) gives

$$y=\frac{d'}{d}=\mathrm{B}^2\left\{\frac{1}{1-r^2}-\frac{k}{\mathrm{D}}(\sin 2\beta-r^2\sin\overline{2\beta-2\kappa})\right\}; \quad . \quad (26)$$

which is the working formula for comparison with the experimental results.

35. Regarding this expression physically, we may note that its essence is the factor B^2, the square of the amplitude transmitted. The denominator $1-r^2$ of the first term in the brackets is due to the repeated coursings of the waves to and fro between the condenser and oscillator. Finally, the second term, which vanishes with k, or with β and κ, is a small correction whose existence is due to the fact that with a damped wave-train the electrometer-throw varies slightly with the phase at the head, as shown in Art. 29.

36. *Stationary Waves at Electrometer.*—Now suppose the electrometer to be at a point on the line distant l_1 cm. from its beginning at the oscillator, and let the condenser be at $l_1+l_2=l$ cm. from the beginning, *i. e.* l_2 cm. beyond the electrometer. This disposition is exhibited in fig. 1. Let the absorbing bridge be at the end of the line as before. Take the origin of coordinates at the electrometer, and let the incident wave-train be represented by

$$\phi_1=e^{-kp(t-x/v)-\sigma x}\cos p(t-x/v), \quad . \quad . \quad . \quad (27)$$

which accordingly becomes at the electrometer

$$\phi_1=e^{-kpt}\cos pt. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The notation previously used for the various wave-trains and for the coefficients of reflexion and transmission will be retained, and the following abbreviations used:—

$l_2/v=t_2, \qquad 2pl_2/v=2pt_2=\theta,$
$\mathrm{A}e^{-2l_2\sigma}=s, \qquad \alpha+\gamma=\kappa,$
$\mathrm{CA}e^{-2l\sigma}=r, \qquad \mathrm{CA}e^{-2l_1\sigma}=r_1,$
$1-2r^2\cos 2\kappa+r^4=\mathrm{D}, \qquad 1-2r_1^2\cos 2\kappa+r_1^4=\mathrm{D}_1.$

37. Then we have as before, if d be the electrometer-throw with no condenser on the line,

$$\mathrm{E}d=\int_0^\infty[e^{-kpt}\cos pt]^2dt,$$

whence

$$4kp(1+k^2)\mathrm{E}d=1+2k^2, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

or, neglecting k^2,

$$4kp\mathrm{E}d=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

38. Now suppose the condenser placed on the line and consider the effect at the electrometer of a single interference of the initial wave-train incident on the condenser with that reflected from the condenser. This is obviously represented by the following integrals :—

$$\int_0^{2t_2} \phi_1^2 dt + \int_{2t_2}^{\infty} (\phi_1 + \phi')^2 dt$$

$$= \int_0^{\infty} \phi_1^2 dt + \int_{2t_2}^{\infty} \phi'^2 dt + 2\int_{2t_2}^{\infty} \phi_1\phi' dt$$

$$= \frac{\mathrm{F}_1 + \mathrm{G}_1 + \mathrm{H}_1}{4kp(1+k^2)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where $\frac{\mathrm{F}_1}{4kp(1+k^2)}$ represents the integral under which it is placed; and the same remark applies to G_1 and H_1.

39. But here again, as in the transmitted system already dealt with, the wave-train first reflected at the condenser returns along the wires, suffering attenuation during its transit, is reflected at the oscillator, and is again attenuated in passing along the line to the electrometer. This second wave-train produces a second interference phenomenon, like that due to the initial wave already treated ; but phase changes have been introduced and the amplitude diminished. Evidently, then, to complete the account of what happens at the electrometer, and frame a theory of the throw d' to be expected, we need an infinite decreasing series of integrals of each of the three types given in (31) as due to the first interference effect.

40. All these integrals, when evaluated, have the same denominator ; hence bringing that to the left side of the

equation, we may write

$$\left.\begin{aligned}4kp(1+k^2)\mathrm{E}d' = {} & \mathrm{F}_1+\mathrm{G}_1+\mathrm{H}_1\\ & +\mathrm{F}_2+\mathrm{G}_2+\mathrm{H}_2\\ & +\mathrm{F}_3+\mathrm{G}_3+\mathrm{H}_3\\ & +\;.\;.\;.\;.\;.\;.\;.\;.\\ & +\;.\;.\;.\;.\;.\;.\;.\;.\\ & +\;.\;.\;.\;.\;.\;.\;.\;.\\ = {} & \mathrm{F}+\mathrm{G}+\mathrm{H};\end{aligned}\right\} \quad . \;.\;.\; (32)$$

where $\mathrm{F}=\mathrm{F}_1+\mathrm{F}_2+\mathrm{F}_3+\ldots;$

and the same applies to G and H.

41. In constructing the integrals for the first line, we have to note that the reflexion at the condenser and the return of the waves to the electrometer introduce the space coordinate $2l_2$ in two exponential factors and in the argument of the cosine, besides introducing the amplitude factor A and the phase change α.

Again, in passing down any one of the columns in (32) we have to affect each succeeding line by the factor r^2, and introduce κ in the angles whose cosines are taken.

We thus obtain the following scheme of integrals :—

$$\left.\begin{aligned}\mathrm{E}d' = {} & \int_0^\infty e^{-2kpt}\cos^2 pt\,dt + s^2\int_{2t_2}^\infty e^{-2kp(t-2t_2)}\cos^2(p\,.\,\overline{t-2t_2}+\alpha)\,dt\\ & +2s\int_{2t_2}^\infty e^{-2kp(t-t_2)}\cos pt\cos(p\,.\,\overline{t-2t_2}+\alpha)\,dt\\ & +r^2\int_0^\infty e^{-2kpt}\cos^2(pt+\kappa)\,dt + r^2s^2\int_{2t_2}^\infty e^{-2kp(t-2t_2)}\cos^2(p\,.\,\overline{t-2t_2}+\alpha+\kappa)\,dt\\ & +2r^2s\int_{2t_2}^\infty e^{-2kp(t-t_2)}\cos(pt+\kappa)\cos(p\,.\,\overline{t-2t_2}+\alpha+\kappa)\,dt\\ & +\;.\;.\;.\;.\;.\;.\quad +\;.\;.\;.\;.\quad +\;.\;.\;.\;.\;.\\ & +\;.\;.\;.\;.\;.\;.\quad +\;.\;.\;.\;.\quad +\;.\;.\;.\;.\;.\end{aligned}\right\} (33)$$

to an infinite number of lines.

42. All the above integrals are included in the following typical form:—

$$\left.\begin{aligned}\int_{2t_2}^{\infty} & e^{-2kp(t-t_2)}\cos(pt+\delta)\cos(\overline{pt-2t_2}+\delta+\epsilon)\,dt \\ &= \frac{e^{-k\theta}}{4kp(1+k^2)}\Big\{\cos(\theta-\epsilon)-k\sin(\theta+2\delta+\epsilon) \\ &\qquad -k^2(\cos\overline{\theta-\epsilon}+\cos\overline{\theta+2\delta+\epsilon})\Big\}\end{aligned}\right\} \quad (34)$$

And the series to which the columns in (32) and (33) when evaluated give rise are of the type given in equation (24). The evaluation of (33) then yields

$$4kp(1+k^2)\mathrm{E}d'=\mathrm{F}+\mathrm{G}+\mathrm{H}, \quad . \quad . \quad . \quad . \quad (35)$$

where

$$\mathrm{F}=\frac{1}{1-r^2}-\frac{k}{\mathrm{D}}r^2\sin 2\kappa+\frac{k^2}{1-r^2}+\frac{k^2}{\mathrm{D}}(1-r^2\cos 2\kappa), \quad . \quad (36)$$

$$\begin{aligned}\mathrm{G}=s^2\Big\{&\frac{1}{1-r^2}-\frac{k}{\mathrm{D}}(\sin 2\alpha+r^2\sin\overline{2\kappa-2\alpha}) \\ &+\frac{k^2}{1-r^2}+\frac{k^2}{\mathrm{D}}(\cos 2\alpha-r^2\cos\overline{2\kappa-2\alpha})\Big\}, \quad . \quad . \quad (37)\end{aligned}$$

$$\begin{aligned}\mathrm{H}=2se^{-k\theta}\Big\{&\frac{\cos\theta-\alpha}{1-r^2}-\frac{k}{\mathrm{D}}(\sin\overline{\theta+\alpha}-r^2\sin\overline{\theta+\alpha-2\kappa}) \\ &+\frac{k^2\cos\overline{\theta-\alpha}}{1-r^2}+\frac{k^2}{\mathrm{D}}(\cos\overline{\theta-\alpha}-r^2\cos\overline{\theta+\alpha-2\kappa})\Big\}. \quad (38)\end{aligned}$$

43. *Discussion of Interference Phenomena.*—Let us now consider the various features of this result and their physical interpretation. In equations (36) to (38) the values of F, G, and H are arranged in terms commencing with one of the order unity and proceeding by ascending powers of k. The terms involving k are all small as their coefficients are of the order unity, and k is less than 0·1 in the experimental case under examination. Those involving k^2 will be omitted finally as their coefficients are likewise of the order unity.

The presence of the terms in k is due to the fact, already discussed in art. 29, that the electrometer-throw is slightly affected by the phase at the head of a wave-train of given amplitude, period, and damping. They are therefore but small corrections to the main features of the case which are represented by the first terms only of each of the expressions in (36) to (38) for F, G, and H. The denominators of these terms supply the correction for the successive arrivals at the electrometer of wave-trains which have suffered reflexion at the condenser and oscillator and passed to and fro along the line.

44. Let curves be imagined with l_2, the distance between electrometer and condenser, as abscissæ, and F, G, and H as ordinates. It is then seen by inspection of (36) that the curve for F is practically a straight line parallel to the axis of abscissæ. This was to be expected on physical grounds, for it represents the effect at the electrometer due to all the positively-travelling waves. And they are almost independent of any change in the value of l_2 when that change is small compared with l_1.

45. Similarly, on inspection of (37), we see that, apart from the small terms in k and the slight change of r with l_2, the curve for G is a logarithmically drooping one. But the droop is very slight for $s^2 = A^2 e^{-4l_2\sigma}$. This again is what might be expected from physical considerations, since this term, G, is due to the return of the wave-train reflected at the condenser apart from interference effects.

46. Turning finally to equation (38), we see that the main features of H are those represented by the first term. This term consists essentially of two factors, one exponential and the other trigonometrical. The exponential factor here gives a much quicker droop than that in G, for we now have $se^{-k\theta}$ instead of s^2 simply as before.

47. The essential nature of H will be made clearer if we write the chief parts of its first term in full. Thus

$$2Ae^{-2kpl_2/v}\cos\left(\frac{2pl_2}{v}-\alpha\right)=h \text{ (say)}. \quad . \quad . \quad (39)$$

Let now a curve be plotted with h as ordinates and l_2 as abscissæ, and call this the *interference curve*, since it represents the essential features of the electrometer-throws due to interference of waves reflected by the condenser with those incident upon it. Then by inspection of (39) and comparison with equation (27), representing the incident wave-train, we have the following results :—

(1) The interference curve is of *damped wave-form.*

(2) The *wave-length* of the interference curve is *half* that of the incident wave-train.

(3) The *logarithmic decrement per wave* of the interference curve is *equal* to that of the incident wave-train.

(4) The *amplitude* of the interference curve is *double* the amplitude factor introduced by the condenser on reflexion.

(5) The *phase change* exhibited in the interference curve compared with the incident wave-train is *equal in magnitude but opposite in sign* to that introduced by the condenser on reflexion.

48. It may be noted here also in corroboration of these results that, if we simplify to the case of a resistance-bridge of resistance infinity or zero and omit all small terms and corrections, we obtain Bjerknes' expression for interference*.

Thus taking only the first terms of F, G, and H, omitting their denominators and the factor $e^{-z/_{2}\sigma}$, and writing A=1, and $\alpha=0$ or π, we have

$$F+G+H=2(1\pm e^{-k\theta}\cos\theta), \quad . \quad . \quad . \quad (40)$$

which is equivalent to Bjerknes' equation just quoted.

49. If we now simplify equations (35) to (38) by neglect of k^2 and divide by the corresponding equation (30), we obtain

$$\left.\begin{aligned}
&\qquad y=\frac{d'}{d}=F+G+H,\\
&\text{where}\\
&F=\frac{1}{1-r^2}-\frac{k}{D}r^2\sin 2\kappa,\\
&G=s^2\left\{\frac{1}{1-r^2}-\frac{k}{D}(\sin 2\alpha+r^2\sin 2\gamma)\right\},\\
&H=2se^{-k\theta}\left\{\frac{\cos\overline{\theta-\alpha}}{1-r^2}-\frac{k}{D}(\sin\overline{\theta+\alpha}-r^2\sin\overline{\theta+\alpha-2\kappa})\right\}.
\end{aligned}\right\} \quad (41)$$

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* Wied. *Ann.* xliv. pp. 513–526 (1891). Equation near top of page 517.

This is the general formula to the desired degree of accuracy.

50. *Reflected System.*—In order to realize an experimental arrangement by which the value of A, the amplitude factor on reflexion at the condenser, may be inferred as simply as possible, let l_2 be taken very large. The term H is then practically extinguished by its very small exponential factor. But, lest its value should still be appreciable, let two values of l_2 be used, viz.: $l_2+\lambda/8$ and $l_2-\lambda/8$, where λ is the wave-length of the incident waves. These values of l_2 will give to H opposite algebraical signs, and since H is here very small the difference between its values for each position will be quite negligible. Moreover the values of F and G are almost the same for $l_2+\lambda/8$ and $l_2-\lambda/8$. We may, accordingly, write as the working formula for the reflected system,

$$\text{mean } y = \mathrm{F}+\mathrm{G}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (42)$$

the 'mean y' in the experimental case being the arithmetic mean of the ratios $\frac{d'}{d}$ obtained with $l_2+\lambda/8$ and $l_2-\lambda/8$, and F and G may be calculated from (41) as for l_2 simply.

51. *Detection of Phase Change of Reflected Waves.*—We have just noticed a method of practically extinguishing H to simplify the determination of A. Now to determine the phase-change, α, we must take exactly the opposite course and make H paramount, since this term represents the interference phenomena which alone involve α except in a subordinate degree.

We therefore choose a number of values of l_2 differing by small amounts and ranging from zero to about two wave-lengths of the interference-curve.

Since in these cases l_2 is very small compared with l_1 (say 0 to 10 metres and 100 metres respectively), the variable $l=l_1+l_2$ may be put equal to the constant l_1 without material loss of accuracy. Consequently r is replaced by r_1 and D becomes D_1.

52. We thus obtain from (41), under these simplifications, our interference formula, viz.:—

$$\left.\begin{aligned}
&y=\frac{d'}{d}=\mathrm{F}+\mathrm{G}+\mathrm{H},\\
&\text{where}\\
&\mathrm{F}=\frac{1}{1-r_1^2}-\frac{k}{\mathrm{D}_1}r_1^2\sin 2\kappa,\\
&\mathrm{G}=s^2\left\{\frac{1}{1-r_1^2}-\frac{k}{\mathrm{D}_1}(\sin 2\alpha+r_1^2\sin 2\gamma)\right\},\\
&\text{and}\\
&\mathrm{H}=2se^{-k\theta}\left\{\frac{\cos\overline{\theta-\alpha}}{1-r_1^2}-\frac{k}{\mathrm{D}_1}(\sin\overline{\theta+\alpha}-r_1^2\sin\overline{\theta+\alpha-2\kappa})\right\}.
\end{aligned}\right\}\quad(43)$$

53. A further simplification is made in the actual calculation and plotting of the theoretical curve, by writing

$$\mathrm{H}=\frac{2se^{-k\theta}}{1-r_1^2}(1+n)\cos(\theta-\alpha+\nu).\quad .\quad .\quad .\quad(44)$$

The small quantities n and ν are defined as functions of k, r_1, and κ by the identity of these two expressions for H. Both n and ν vanish for $k=0$, and assume a simplified value for $\kappa=0$. The actual values of n and ν in any numerical case can be readily found with sufficient accuracy by the graphical composition of sine and cosine functions, the amplitudes being represented by the lengths of lines whose inclination denotes the relative phase of the respective vibrations.

54. *Interference by Reflexion from a Resistance.*—To obtain the interference effect produced by an intermediate resistance-bridge placed on the line beyond the electrometer we have simply to introduce its constants from equation (11) into equation (43). This substitution gives

$$\left.\begin{aligned}
&y=\frac{d'}{d}=\mathrm{F}+\mathrm{G}+\mathrm{H},\\
&\text{where}\\
&\mathrm{F}=\frac{1}{1-r_1^2}-\frac{k}{\mathrm{D}_1}r_1^2\sin 2\gamma,\\
&\mathrm{G}=s^2\left\{\frac{1}{1-r_1^2}-\frac{k}{\mathrm{D}_1}r_1^2\sin 2\gamma\right\},\\
&\text{and}\\
&\mathrm{H}=2se^{-k\theta}\left\{\frac{\cos\overline{\theta+\pi}}{1-r_1^2}+\frac{k}{\mathrm{D}_1}(\sin\theta-r_1^2\sin\overline{\theta-2\gamma})\right\}\\
&\quad=\frac{2se^{-k\theta}}{1-r_1^2}(1+n)\cos(\theta+\pi+\nu).
\end{aligned}\right\}\quad(45)$$

For a no-resistance bridge this is further simplified by the amplitude factor being unity.

EXPERIMENTS.

55. *Positions of Condensers.*—For the transmitted system the condensers were placed at FF′ (fig. 1, p. 275), the distance SF being 59 metres $\pm\lambda/8$. These *two* distances were chosen to eliminate any error which would arise if interference occurred on the oscillator side of the condenser. This might conceivably take place between the head of a wave-train arriving at the condenser simultaneously with the departure of the tail of a previous train reflected there. To reduce this anticipated disturbance to a minimum, the distance SF was chosen of the order 60 m. in preference to any smaller distance. It is easily seen that if this interference was additive in one of the positions chosen, then it would be subtractive in the other, and both being small the arithmetic mean could be taken. From the tables of readings it may be noted that neither of these precautions was unnecessary.

56. In the reflected system the distance ED of the condenser beyond the electrometer, denoted by l_2 in the theory, was made 48 m. $\pm\lambda/8$; the two positions being again adopted to obviate any error due to interference. Here again the precautions were not in vain. The wave-length λ of the incident waves was determined by Bjerknes' method to be 8·5 m.

For the interference phenomena, observed in order to detect the phase change on reflexion, the distance ED was varied by half a metre from 0·75 m. to about 8·0 m. so as to furnish nearly two wave-lengths of the interference curve.

The methods of taking the readings and their results will be sufficiently understood from the following tables and accompanying curves. The three condensers used were chosen by reference to the curve in fig. 5 as likely to yield typical results.

57. *Large Condenser.*—Disks 15 centim. radius and placed 1 centim. apart.

(i.) *Transmitted System.* On taking seven readings without condenser on alternated with six readings with condenser on, the values were respectively of the order

whence

$$\left.\begin{aligned} d=26{\cdot}8 \text{ and } d'=2{\cdot}6 \\ y=\frac{d'}{d}={\cdot}097 \text{ nearly} \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (46)$$

With such small readings as those here obtained for d' it cannot be professed that they are free from errors due to small variations of the zero, which is never quite steady and

TABLE II.—Reflected System for Large Condenser.

Electrometer-Throws, d, without Condenser on.		Electrometer-Throws, d', with Condenser at l_2 beyond Electrometer.		Ratio of Throws, $\frac{d'}{d}$, for each position, viz.:	
Actual Throws.	Interpolated Means.	$l_2=48^{\mathrm{m}}-\lambda/8$.	$l_2=48^{\mathrm{m}}+\lambda/8$.	$l_2=48^{\mathrm{m}}-\lambda/8$.	$l_2=48^{\mathrm{m}}+\lambda/8$.
23	23	45		1·957	
23	22·5		42		1·867
22	22	44		2·000	
22	22		42		1·909
22	25	50		2·000	
28	25·5		50		1·961
23	24	49		2·042	
25	25		54		2·160
25	27·5	56		2·036	
30	29·5		58		1·966
29	29·5	60		2·034	
30	29		57		1·966
28	28	59		2·107	
28	28		55		1·964
28	26	54		2·077	
24	26		54		2·077
28	29	50		1·724	
30	28·5		49		1·719
27	24·5	50		2·041	
22	20·5		43		2·098
19					
Mean Values of Ratios				2·002	1·969
Whence Final Value or Mean of Means = 1·986.					

Note.—This set of observations occupied 2 hours 45 minutes, during which time the zero crept 22 scale-divisions in the positive direction, viz., from −32 to −10.

is always read before each throw is taken throughout all the experimental work.

(ii.) *Reflected System.* Two sets of 41 readings each were taken for this arrangement. The first gave

$$\text{mean } y = \frac{\text{mean } d'}{d} = 1{\cdot}862. \quad . \quad . \quad . \quad . \qquad (47)$$

The second, in which the behaviour of sparks and electrometer was more regular, gave

$$\text{mean } y = \frac{\text{mean } d'}{d} = 1{\cdot}986. \quad . \quad . \quad . \quad . \qquad (48)$$

This second set of readings is given in Table II. (p. 298).

(iii.) *Interference System.* Four sets of readings were taken with this arrangement of the apparatus. The last of these is given in Table III., and the points corresponding to all of them are plotted in fig. 6, a curve is then drawn through the mean position to represent as fairly as may be the result of all the readings.

TABLE III.—Interference System for Large Condenser.

Electrometer-Throws, d, without Condenser on.		Condenser on Line.		Ratios, $\frac{d'}{d}=y$, of Throws with and without Condenser.
Actual Readings.	Interpolated Means.	Electrometer Throws, d'.	Distance, l_2, of Condenser beyond Electrometer.	
33	30	29	0·75 m.	0·97
27	29·5	53	1·0	1·80
32	28·5	72	1·5	2·53
25	25·5	112	2·0	4·39
26	16 *	67	2·5	4·19
16	17	64	3·0	3·76
18	18	48	3·5	2·67
18	19·5	32	4·0	1·64
21	22	29	4·5	1·32
23	25	82	6·25	3·28
27	27	86	7·0	3·19
27	26	64	7·5	2·46
25	22·5	48	8·0	2·13
20				

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* A pause was made here to adjust balls of spark-gap in oscillator; hence the 26 is disregarded, and 16 taken as true reading.

Since the amplitude factor of the wave-train reflected from this condenser is almost unity, a bridge of no-resistance, whose reflexion factor is exactly unity, was used as a comparison and to show the phase-difference between the two curves. Three sets of readings were taken with this bridge, the points and mean curve for which are plotted on fig. 7.

Fig. 6.—Experimental Results:—Interference System for Large Condensers. First three sets of readings indicated by •, o, and † respectively. Fourth Set (Table III.) by ×.

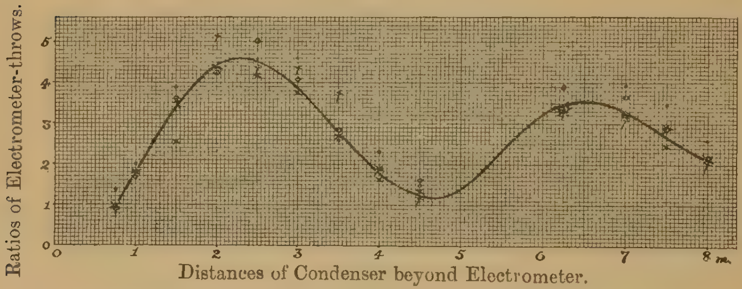
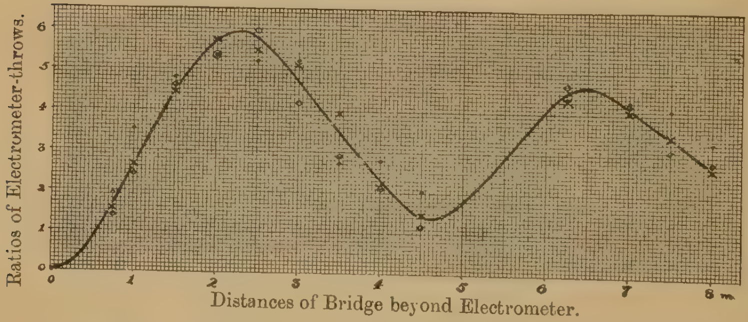


Fig. 7.—Experimental Results:—Interference System for Bridge of Negligible Resistance. Three sets of readings indicated by •, o, and × respectively.



58. *Medium Condenser.*—Disks 9 centim. radius and placed 1 centim. apart.

(i.) *Transmitted System.* The readings for this arrangement result in the ratio

$$\text{mean } y = \frac{\text{mean } d'}{d} = 0{\cdot}349. \quad . \quad . \quad . \quad . \quad (49)$$

The readings are shown in Table IV.

Table IV.

Transmitted System for Medium Condenser.

Electrometer-Throws, d, without Condenser on.		Electrometer Throws, d', with Condenser at l beyond Oscillator, where		Ratios of Throws, $\frac{d'}{d}$, for each position, viz. :—	
Actual Throws.	Interpolated Means.	$l=59^m-\lambda/8$.	$l=59^m+\lambda/8$.	$l=59^m-\lambda/8$.	$l=59^m+\lambda/8$.
28	27·5	10		0·364	
27	30		10		0·333
33	31	11		·355	
29	29·5		10		·339
30	30	11		·367	
30	29·5		10		·339
29	28	9		·321	
27	25		7		·280
23	24·5	9		·367	
26	26		8		·308
26	25	9		·360	
24	23·5		8		·340
23	23	8		·348	
23	22·5		8		·356
22	22	8		·364	
22	22		7		·318
22	21	8		·381	
20	20		8		·400
20	20·5	7		·341	
21	20		8		·400
19					
		Arithmetic Means......		0·357	0·341
		Whence Mean of Means = 0·349.			

(ii.) *Reflected System.* For this arrangement two sets each of 41 readings were taken. The first set gave

$$\text{mean } y=\frac{\text{mean } d'}{d}=1\cdot523\,; \quad . \quad . \quad . \quad . \quad (50)$$

the second set gave

$$\text{mean } y=\frac{\text{mean } d'}{d}=1\cdot626\,; \quad . \quad . \quad . \quad . \quad (51)$$

the readings being contained in Table V.

TABLE V.

Reflected System for Medium Condenser.

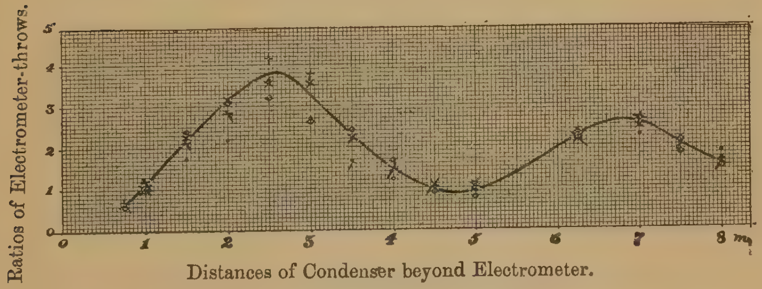
Electrometer-Throws, d, without Condenser on.		Electrometer-Throws, d', with Condenser at l_2 beyond Electrometer.		Ratio of Throws, $\frac{d'}{d}$, for each position.	
Actual Throws.	Interpolated Means.	$l_2 = 48^m - \lambda/8$.	$l_2 = 48^m + \lambda/8$.	$l_2 = 48^m - \lambda/8$	$l_2 = 48^m + \lambda/8$.
25	25	42		1·680	
25	26		42		1·615
27	26·5	46		1·736	
26	28·5		53		1·860
31	29·5	55		1·864	
28	29		50		1·724
30	31	54		1·742	
32	33		54		1·636
34	33·5	52		1·552	
33	33		50		1·515
33	32	51		1·594	
31	30·5		47		1·541
30	30	49		1·633	
30	30		47		1·567
30	30	50		1·667	
30	29		44		1·517
28	28·5	42		1·474	
29	28		44		1·571
27	26·5	42		1·585	
26	23		33		1·435
20					
		Arithmetic Means.........		1·653	1·598
		Whence Mean of Means = 1 626.			

(iii.) *Interference System.* For this disposition of the apparatus four sets of readings were taken. One of these is given in Table VI. On fig. 8 are plotted the points from all the readings, and the curve through their mean position is shown also.

TABLE VI.—Interference System for Medium Condenser.

Electrometer-Throws, d, without Condenser on.		Condenser on Line.		Ratios, $\frac{d'}{d}=y$, of Throws with and without Condenser.
Actual Throws.	Interpolated Means.	Electrometer Throws, d'.	Distances, l_2, of Condenser beyond Electrometer.	
			m.	
37	36·5	22	0·75	0·60
36	33	36	1·0	1·09
30	32	73	1·5	2·28
34	33·5	105	2·0	3·13
33	32·5	115	2·5	3·54
32	32	113	3·0	3·53
32	34	75	3·5	2·21
36	34·5	51	4·0	1·48
33	30·5	35	4·5	1·15
28	30·5	32	5·0	1·05
33	34·5	82	6·25	2·38
36	34·5	85	7·0	2·46
33	32·5	70	7·5	2·15
32	33·5	54	8·0	1·61
35				

Fig. 8.—Experimental Results. Interference System for Medium Condenser. The several sets of readings are respectively indicated by •, ○, †, and ×.



59. *Small Condenser.*—Disks 5 centim. radius and placed 1 centim. apart.

(i.) *Transmitted System.* For this arrangement the set of 41 readings shown in Table VII. was taken. These readings yield the result

$$y=\frac{d'}{d}=0{\cdot}868. \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

TABLE VII.—Transmitted System for Small Condenser.

Electrometer-Throws, d, without Condenser on.		Electrometer Throws, d', with Condenser at l beyond Oscillator, where		Ratio of Throws, $\frac{d'}{d}$, for each position, viz.:	
Actual Throws.	Interpolated Means.	$l=59^m-\lambda/8$.	$l=59^m+\lambda/8$.	$l=59^m-\lambda/8$.	$l=59^m+\lambda/8$.
20	21	15		0·714	
22	22·5		15		0·667
23	24	20		·833	
25	23		18		·783
21	23	19		·826	
25	23·5		21		·894
22	22	19		·864	
22	22·5		19		·844
23	20·5	19		·927	
18	16		14		·875
14	16	14		·875	
18	18 5		14		·757
19	18	18		1·000	
17	17·5		16		·914
18	18·5	17		0·919	
19	17		17		1·000
15	16	14		·875	
17	17·5		14		0·800
18	15	16		1·067	
12	12		11		·917
12					
Arithmetic Means				0·890	0·845
Whence Mean of Means = 0 868					

(ii.) *Reflected System.* For this arrangement two sets each of 41 readings were taken. The first set gave

$$\text{mean } y = \frac{\text{mean } d'}{d} = 1{\cdot}168. \quad . \quad . \quad . \quad . \quad (53)$$

The second set of readings is given in Table VIII. and yields the result

$$\text{mean } y = \frac{\text{mean } d'}{d} = 1{\cdot}188. \quad . \quad . \quad . \quad . \quad (54)$$

TABLE VIII.—Reflected System for Small Condenser.

Electrometer-Throws, d, without Condenser on.		Electrometer-Throws, d', with Condenser at l_2 beyond Electrometer.		Ratios of Throws, $\frac{d'}{d}$, for each position.	
Actual Throws.	Interpolated Means	$l_2 = 48^{\text{m}} - \lambda/8$.	$l_2 = 48^{\text{m}} + \lambda/8$.	$l_2 = 48^{\text{m}} - \lambda/8$.	$l_2 = 48^{\text{m}} + \lambda/8$.
37	32·5	37		1·138	
28	24·5		29		1·184
21	14·5	19		1·310	
*{ 8 32	33·5		35		1·045
35	34	41		1·206	
33	31·5		37		1·175
30	32	39		1·219	
34	32		36		1·125
30	31·5	40		1·270	
33	33·5		38		1·134
34	31·5	39		1·238	
29	31		37		1·194
33	32·5	40		1·231	
32	33		37		1·121
34	32·5	39		1·200	
31	32·5		38		1·169
34	33·5	39		1·164	
33	33		37		1·121
33	32·5	41		1·262	
32	32		40		1·250
32					
Arithmetic Means				1·224	1·152
Whence Mean of Means is .... 1·188.					

* The balls of the spark-gap of the primary oscillator were adjusted between these two readings.

(iii.) *Interference System.* With the apparatus arranged for observing the interference phenomena with this condenser, three sets of readings were taken. One of these is shown in Table IX. It will be seen to include readings for a *resistance-bridge* also. This bridge consisted of graphite markings upon a half disk of ground glass 3 inches diameter, and was made of a resistance of 235 ohms, the value calculated to give the same amplitude factor on reflexion as the condenser

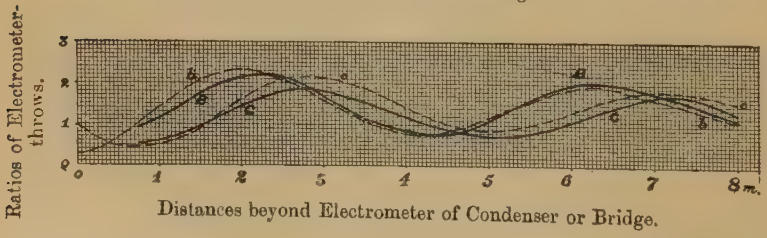
TABLE IX.—Interference System for Small Condenser and Corresponding Resistance Bridge.

Electrometer-Throws, *d*, without either Condenser or Resistance Bridge on.		Electrometer-Throws, *d'*, with apparatus at l_2 beyond Electrometer, viz.:—		Values of the Distance l_2 beyond Electrometer at which Condenser or Resistance Bridge is placed.	Ratios of Throws, $\frac{d'}{d}$, obtained with	
Actual Throws.	Interpolated Means.	Condenser on Line.	Resistance Bridge on Line.		Condenser.	Resistance Bridge.
				m.		
27	26	34	27	8·0	1·31	1·04
25	26	42	39	7·5	1·62	1·50
27	25	42	43	7·0	1·68	1·72
23	24·5	31	48	6·25	1·27	1·96
26	26	19	27	5·0	0·73	1·04
26	25·5	22	19	4·5	0·86	0·75
25	24	30	20	4·0	1·25	0·83
23	23·5	40	25	3·5	1·70	1·06
24	23	43	41	3·0	1·87	1·78
22	22	39	45	2·5	1·77	2·05
22	22	30	43	2·0	1·36	1·95
22	19	18	35	1·5	0·95	1·84
16	14	10	14	1·0	0·71	1·00
12	13·5	8	12	0·75	0·59	0·89
15						

now in use. This resistance was tested, and if necessary adjusted to 235 ohms, immediately before each time it was used.

Table X. gives a summary of the results, for both condenser and resistance-bridge, of all three sets of readings.

Fig. 9.—Interference Systems for Small Condenser and for Bridge of 235 ohms Resistance. Experimental results in full lines, theoretical curves in broken lines. C and *c* denote curves for Condenser. B and *b* denote those for Bridge.



From the mean values thus obtained the experimental curves for condenser and resistance-bridge are plotted in fig. 9.

Table X.—Summary of Results for Interference System with Small Condenser and Corresponding Resistance Bridge.

Ratios, $\frac{d'}{d}$, with the Condenser on the Line.				Values of the Distances l_2 beyond Electrometer at which Condenser or Resistance Bridge is placed.	Ratios $\frac{d'}{d}$, with the Resistance Bridge on the Line.			
Separate Values.			Means.		Means.	Separate Values.		
(A)	(B)	(C)		m.		(C)	(B)	(A)
0·526	0·39	0·59	0·50	0·75	0·90	0·89	0·89	0·912
·604	·48	·71	·60	1·0	1·11	1·00	1·13	1·208
·898	·95	·95	·93	1·5	1·76	1·84	1·87	1·551
1·333	1·57	1·36	1·42	2·0	2·05	1·95	2·03	2·157
1·885	1·56	1·77	1·74	2·5	2·15	2·05	2·10	2·308
1·738	1·79 1·59	1·87	1·75	3·0	1·45	1·78	1·36 1·02	1·639
1·486	1·20	1·70	1·46	3·5	1·19	1·06	1·13	1·371
1·206	1·50	1·25	1·38	4·0	0·97	0·83	1·11	0·971
0·812	0·93	0·86	0·87	4·5	0·81	0·75	0·96	0·719
·926	·68	·73	·78	5·0	1·05	1·04	1·03	1·074
1·309	1·24	1·27	1·27	6·25	2·02	1·96	1·97	2·145
1·569	1·66	1·68	1·64	7·0	1·75	1·72	1·87	1·662
1·636	1·73	1·62	1·66	7·5	1·45	1·50	1·48	1·364
1·118	1·45	1·31	1·29	8·0	1·15	1·04	1·18	1·235

The letters (A), (B), and (C) at the heads of the columns of separate values show corresponding sets of readings for Condenser and Resistance-bridge.

Comparison of Theory and Experiment.

60. *Transmitted and Reflected Systems.*—The comparison of theoretical and experimental results for the transmitted and reflected systems of all three condensers is exhibited in Table XI.

The data for the theoretical values of the ratios are as follows.

The Reflexion and Transmission Constants for the three condensers are those given in fig. 5 and in the lower part of Table I.

The Amplitude Factor, C, for the oscillator is taken as 0·716 from the experiments * made in 1898 on the very line now in use.

The Attenuation Constant, σ, was also taken, from the experimental determinations of the paper just quoted, as equal to 0·0000130.

TABLE XI.

Comparison of Theory and Experiment for Transmitted and Reflected Systems of all three Condensers.

Condenser and System of Waves observed.		Values of Ratios, $\frac{d'}{d}$, of Electrometer-Throws with and without Condenser.		
		Calculated by Approximate Theory from equations (26) and (42).	Experimentally determined Values.	Calculated by Approximate Theory with corrections from equations (56) and (57).
Large.	Transmitted.	0·079	0·097 (?)	0·108
	Reflected.	2·236	1·924	2·095
Medium.	Transmitted.	0·420	0·349	0·367
	Reflected.	1·924	1·574	1·754
Small.	Transmitted.	0·966	0·868	0·706
	Reflected.	1·330	1·178	1·178

---

* "Attenuation of Electric Waves along a Line of Negligible Leakage," Phil. Mag. Sept. 1898. See in Table II. (p. 301) the value of ρ, which is the C of the present notation.

The Phase-change, γ, introduced by the oscillator is calculated theoretically as equal to $-23° 28'$.

Other data are :—

$\mathrm{L}v = 56 \times 10^{10}$ C.G.S. E.M. units (calculated and verified experimentally).

$k = 0{\cdot}0955$ as determined experimentally.

$p = 2\pi v/\lambda = 1{\cdot}96 \times 10^8$ radians per second as determined experimentally.

61. It is seen on reference to Table XI. that there is a considerable discrepancy between the experimentally-determined values of the ratios of electrometer-throws and those calculated from the approximate theory. This theory, used as a first working approximation, takes $\iota = 0$ in the original incident wave-train $e^{-kpt} \cos(pt + \iota)$, and omits the exponential term introduced on reflexion at the condenser. This was done because the value of ι is unknown. Let us now determine the *maximum* correction needed to the above theory, the results of which are placed in the last column of Table XI. Assume for ι such values as to make for each condenser $\iota + \beta = 0$. This makes the coefficient of the exponential term a maximum. Further, let us suppose (what is not possible) that the coefficient of the exponential term retains its maximum value all through; *i. e.*, put $\iota + \beta + 2\kappa = 0$ or π, $\iota + \beta + 4\kappa = 0$ or 4π &c. for the successive reflexions and transmissions. In order to convert the time-integral of the square of the amplitude, on the approximate theory, to its true value when the exponential term is retained, let A^2 and B^2 be now replaced by $\rho \mathrm{A}^2$ and $\tau \mathrm{B}^2$ respectively.

Then we shall have

$$\left.\begin{aligned} \rho = \int_0^\infty & [\mathrm{A}e^{-kpt} \cos(pt + \iota + \alpha) - \mathrm{B} \cos(\iota + \beta) e^{-2pt/\chi'}]^2 dt \\ & \div \int_0^\infty [\mathrm{A}e^{-kpt} \cos(pt + \iota + \alpha)]^2 dt, \\ \text{and} \qquad & \\ \tau = \int_0^\infty & [\mathrm{B}e^{-kpt} \cos(pt + \iota + \beta) - \mathrm{B} \cos(\iota + \beta) e^{-2pt/\chi'}]^2 dt \\ & \div \int_0^\infty [\mathrm{B}e^{-kpt} \cos(pt + \iota + \beta)]^2 dt \end{aligned}\right\} \quad (55)$$

where $\iota + \beta$ is to be written equal to zero.

Further, since ι has now a finite value, and different for each condenser, equations (26) and (42) need modifying by the introduction of ι. We thus obtain the following corrected equations:—

For the transmitted system:

$$y=\tau B^2\left\{\frac{1}{1-r^2}-\frac{k}{D}r^2\sin 2\kappa\right\}; \quad . \quad . \quad . \quad (56)$$

and for the reflected system:

$$\text{mean } y=F+\rho G;$$

where

$$\left.\begin{aligned}&F=\frac{1}{1-r^2}-\frac{k}{D}(\sin 2\iota-r^2\sin\overline{2\iota-2\kappa}),\\&\text{and}\\&G=s^2\left\{\frac{1}{1-r^2}-\frac{k}{D}(\sin\overline{2\iota+2\alpha}-r^2\sin\overline{2\iota+2\alpha-2\kappa}),\right\}\end{aligned}\right\}(57)$$

ρ and τ being defined by (55).

62. It is to be noted that these formulæ in *two* respects *over-correct* the original approximate expressions. *First*, they assume that the trigonometrical coefficient of the exponential term is a maximum for *every* successive incidence; and *second*, they assume that for each condenser $\iota+\beta=0$, which necessitates a different ι for each case, whereas the wave-train launched along the line must have the same shaped head in each case. Thus the truth on the long-wave theory may be expected to lie between the values given in the first and third columns of Table XI.

63. In comparing the experimental values with the theory, the following points may be noted :—

(1) In one case (in Table XI.) experiment and theory give identical values (last line).

(2) In two cases the theory seems over-corrected (lines 1 & 5).

(3) In three cases the correction to the theory fails to bring the values down to those experimentally determined.

(4) Hence the outstanding discrepancy is on the side of slightly less reflected and less transmitted than theory

predicts, though further experiments under a greater variety of conditions would be needed to establish this view of the case.

(5) Turning now from the question of the amplitudes of the reflected and transmitted waves to that of the phase-change, α, introduced on reflexion, we see from figs. 9, 10, & 11 that the theoretical and experimental results are in fair agreement.

Fig. 10.—Interference Systems for Large Condenser and for Bridge of Negligible Resistance. Experimental results in full lines, theoretical curves in broken lines. C and *c* denote curves for Condenser; B and *b* denote curves for Bridge.

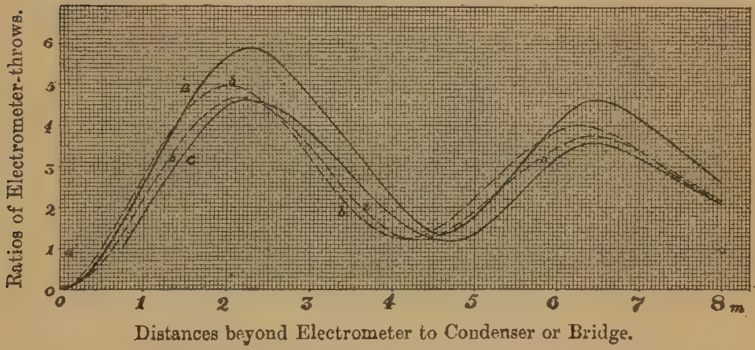
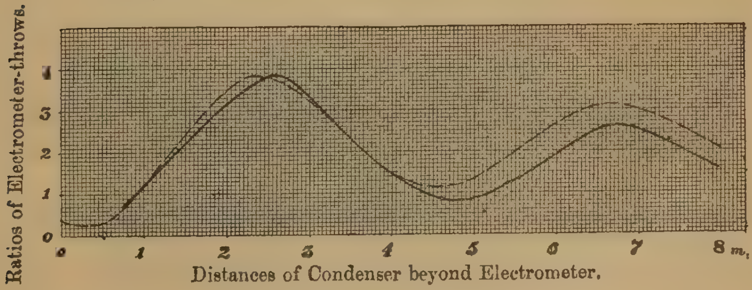


Fig. 11.—Interference System for Medium Condenser. The full line is the Experimental Curve, and the broken line is the Theoretical Curve.



Our indebtedness to the works of Oliver Heaviside, obviously great, has been increased by the receipt in MS. of supplementary elucidations with which Mr. Heaviside has favoured us. This invaluable help we here gratefully acknowledge.

Univ. Coll. Nottingham,
August 1899.

30

XX. *Some Lecture Experiments illustrating Syntony.*

By Philip E. Shaw, *B.A.*, *B.Sc.*[*]

In the Journal of the Institution of Electrical Engineers (Feb. 1899) will be found an account by Prof. Oliver Lodge of his researches in Magnetic Space Telegraphy. The present writer then set up some apparatus to show these methods in a popular lecture. Considerable difficulties soon presented themselves, but success was ultimately attained. Those who are conversant with the above paper will admit that the theory involved in it is of importance, and that any new demonstration of it would be valuable.

Besides the interest attaching to the theory of syntony, this method of magnetic space-telegraphy has promise of practical and commercial value, and has been shown already by Prof. Lodge to work well over considerable distances.

The following brief account contains a notice of the general method, of special details introduced by the author, and of precautions to be adopted.

Theory.

A summary will be given of the more essential points.

I. The frequency (N) of a circuit of capacity S and self-induction L is

$$N=\frac{160}{\sqrt{L\,.\,S}}$$

where L is reckoned in henries and S in microfarads.

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[*] Read March 23, 1900.

II. The mutual induction of two parallel coaxial coils of turns n and m, radii a and b, at distance r apart is, assuming r large,

$$\mathrm{M} = \frac{m\pi a^2 \,.\, n\pi b^2}{r^3}.$$

III. The self-induction of a short flat coil, as used for sending or receiving, is

$$\mathrm{L} = 4\pi\mu n^2 a\left(\log_e \frac{8a}{c} - 2\right),$$

and for a long solenoid (neglecting a small correction for the ends)

$$\mathrm{L} = \frac{4\pi\mu n^2 \mathrm{A}}{l}.$$

$$\left\{\begin{array}{l} n = \text{number of turns ;} \\ a = \text{radius of coil ;} \\ c = \text{radius of wire ;} \\ \mathrm{L} = \text{length of solenoid ;} \\ \mathrm{A} = \text{mean sectional area.} \end{array}\right.$$

IV. Current Amplitude $= \dfrac{\mathrm{E}_0/\mathrm{R}}{\sqrt{1+\dfrac{\mathrm{L}}{\mathrm{SR}^2}\left(\dfrac{p}{p_0}-\dfrac{p_0}{p}\right)^2}}$,

where $\dfrac{p_0}{2\pi}$ = natural frequency of circuit,

$\dfrac{p}{2\pi}$ = frequency of alternating-current in circuit ;

but for exact resonance, the current-amplitude $= \mathrm{E}_0/\mathrm{R}$; hence for *sharp* resonance (since then $p = p_0$), $\dfrac{\mathrm{L}}{\mathrm{SR}^2}$ must be large.

V. Magnification Ratio, due to resonance, is given by the expression

$$\frac{\mathrm{V}}{\mathrm{E}_0} = \frac{p\mathrm{L}}{\mathrm{R}},$$

supposing the damping is small ;

where E_0 = impressed E.M.F. from current source,

V = effective potential-difference at the condenser-terminals.

Now we have as far as possible to arrange the circuits in accordance with the above principles, and where these seem mutually in opposition to make a judicious compromise.

The *desiderata* are :—

(1) R *small*, to obtain large current-amplitude, small damping, sharp resonance, and large magnification-ratio. Notice that R includes hysteresis if an iron core is used, and eddy-currents in neighbouring circuits.

(2) L *large*, to obtain sharp resonance and large magnification-ratio.

(3) S *small*, to obtain sharp resonance and to avoid large sparks at ‘make’ and ‘break.’

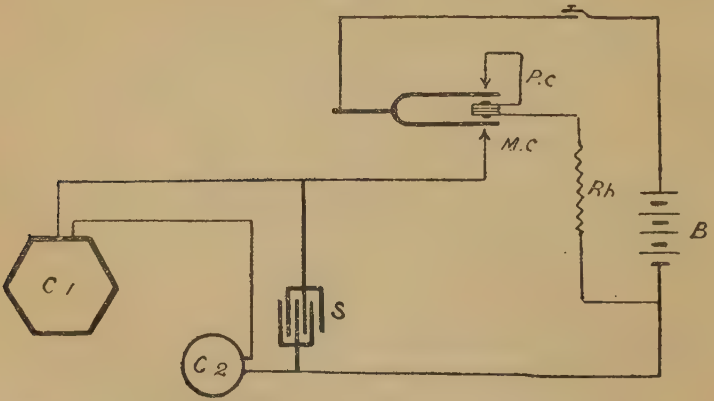
(4) *Radius of sending and receiving coils large*, to obtain large M.

(5) The auxiliary coils must be suited to conditions (1) and (2), otherwise they may have any size or shape. For the comparatively small frequency used, the self-induction part of the impedance need not be considered.

The Circuits.

The sending-circuit is shown in the sketch (fig. 1), which is in elevation. The current leaving the cells at the top end passes through the key, fork, platinum-contact (P.C.), rheostat, and to the lower end of the cells ; the fork is worked by

Fig. 1.



the passage of this current through the electromagnet between the prongs of the fork.

But there is another branch to the circuit, beginning at the mercury-contact (M.C.), then through the coils C_1 and C_2, the adjustable condenser S being put as a shunt to the two coils, then to the lower end of the cells.

Thus if S were removed we should obtain current-alternations in the coils of the frequency (100) of the fork; but with S in place, we have a frequency depending on the values of L and S in the coils. In setting up the system we select suitable coils and condenser, calculating the values of L from the dimensions of the coils; then put in such a value of S as will give the required frequency, and finally adjust to a maximum by the iron core in C_2 (see expression I.).

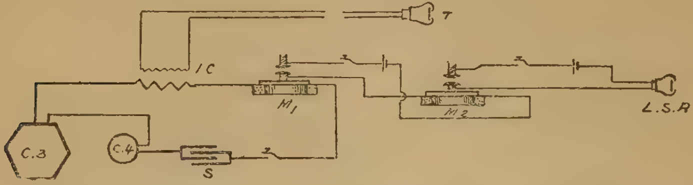
This frequency (400 was used) must be an exact multiple of that of the fork (100), then between each charge received by S from the fork, there would be four complete surgings between S, C_1, C_2 ; the potential changes would be considerable, and violent shocks might be obtained.

L may be varied by the introduction of any number of coils at C_2, or by moving a core of iron wires in C_2. This latter is a convenient adjustment, but wasteful on account of hysteresis. The adjustments are (1) the mercury-contact (M.C.), (2) the rheostat, (3) adjustable L in C_2. Place one ear on the flat condenser (taking care to avoid getting a shock from its terminals), listen to the note heard in it, and change (1), (2), and (3) up to maximum loudness. The adjustment (1) must on no account be neglected ; the method adopted was to have the fork rigidly held, but capable of being rotated by any small amount in a vertical plane.

Thus, as above described, we have a circuit with a given frequency, whose note can be raised to a maximum intensity.

Now turn to the secondary (or receiving) circuit (fig. 2). The coil C_3 is placed parallel to C_1, and catches the waves from it ; C_4 is an auxiliary coil. The condenser S is in series in the circuit, and not, as in the primary, shunted across the ends of the coils. There are two other coils in the same circuit:—(1) M_1 is the coil of the relay, with its microphone-carbons shown above it ; (2) the small resistance-winding of a telephone induction-coil, the large resistance-winding being in series with the telephone T.

Fig. 2.



If now the coil C_3 is taking up the waves from the sending-circuit, and the variables C_4 and S are set for exact tuning (to frequency 400) a note of maximum loudness will be heard in the telephone T. In the primary it is convenient, though wasteful, to have an iron core in a coil for the small adjustment of L, but in the secondary it would be useless, since μ is small for the very weak currents existing.

Now put in the first relay by adjusting the carbons at M_1. The action occurring at M_1 and M_2 must be explained in detail. The coil M_1 lies in a horizontal annular space in which the lines of force run radially, and normal to the wires in the coil; then if current-alternations occur in the coil, it is impelled up and down with the frequency of the alternations; the field meanwhile is maintained constant by a separate strong current (say 10 amps.). The movements of the coil will, by the action of the microphone, produce alternating currents of a higher order of intensity in the relay-coil M_2; and this, in turn, will in like manner give strong currents in the last circuit, producing a loud note in the loud-speaking receiver (L.S.R.). Although, to avoid confusion in the diagram, no such connexions are shown, it is easy to put the induction-coil and telephone (I.C. and T.) into the second circuit, and by them adjust the working of M_1 to a maximum intensity.

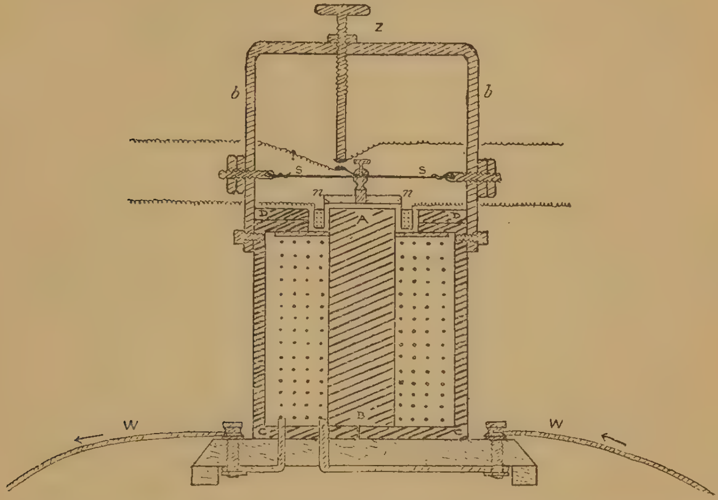
The relays should be guarded from all vibrations by being put on blocks resting on soft rubber balls; also they should be on separate blocks, otherwise the action of one will start the other.

Description of the Relay.

The principle involved is due to Prof. Lodge, and is found in his magnifying-telephone; but the attachments of the coil and the system suspending it are due to the author, and will be shortly described.

The wires WW (fig. 3) carry the strong current (say 10 amps.) used to produce a field ; the magnetic circuit of soft iron is seen to be ABCDA ; it has the air-gap between D and A in which the coil *n n* lies. This is the coil M_1 or M_2 in fig. 2.

Fig. 3.



The coil *n n* is very light, 60 turns of covered copper wire (36 s.w.g.), resistance about 4 ohms, wound on a paper pill-box, which is light and rigid and perfectly circular, and is hence a very convenient former for the coil. The steel wire *s s* has a light brass fitting screwed tightly to its centre ; below this is a light bow of cedar lashed and cemented to the brass above and lashed and cemented to the coil below.

As seen in the sketch, the wire is fixed (bent on itself and brazed) to a brass screw at each end, each provided with two nuts, on the outside of the stout brass frame *b b*.

By tightening the wire we can produce in it the required frequency, 400 (this can be observed by gently tapping the wire and listening for its natural frequency) ; then alternations in the current of *n n* must produce vibration in the wire *s s*, and when the carbons are set by the screw z we have the microphone acting.

Two graphite buttons, or one graphite and one hard carbon button, were found to act very well.

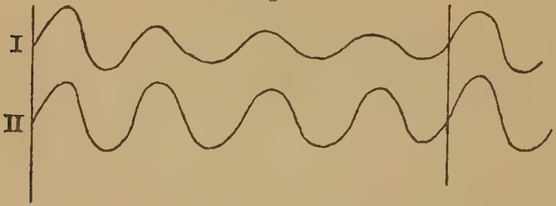
Another form of relay was used. Take a Blake transmitter, change the stiff iron plate for a more yielding one, and attach the coil $n\,n$ to it. This acts fairly, but is obviously not syntonic with the whole system as in the other case.

Manipulation.

The chief special difficulties may be mentioned categorically.

I. It must be borne in mind that in such an apparatus as that used, where the ratio $\frac{R}{L}$ is comparatively large, damping occurs rapidly, and consequently the current-amplitude dies out rapidly between each fresh charge received from the fork.

Fig. 4.



We supposed the fork to have frequency 100, and the circuit to have frequency 400. Then the curve for current would be of the nature shown in I.; whereas the ideal curve, where $\frac{R}{L}$ is negligible, would be as in II., where the amplitude is seen to remain constant. Consequently in our system we should have a pronounced fundamental 100 as well as an harmonic 400, and we have to learn to pick out the latter and, in adjusting the circuit, to work it up to a maximum. This applies to both primary and secondary circuits.

II. Care must be taken to properly adjust the platinum and mercury contacts, not only to produce the maximum true sound in the circuit, but also to avoid any spurting at the contact; this would have its counterpart in violent spurts in the sounds in the coils, which mask the true effect.

III. The greatest difficulty experienced, however, was in the microphones, both (1) in obtaining them truly syntonic with the circuit and with one another, and (2) in the minute adjustment of the carbons for very weak currents. The special relay described above worked well, but requires delicate handling in respect of both (1) and (2). Anyone who has worked a granular transmitter, or indeed any microphone with a view to obtaining *maximum* effects for very small movements, will admit that an exceedingly fine adjustment is required. This might seem to be self-evident, but the author has made independent research on this point, his results being that a movement of one carbon of the order 10^{-5} cm. would carry the microphone from hard contact (no microphone action) to complete freedom. Hence the difficulty above stated is quite intelligible.

In working the relay described previously, the final adjustment was made by gently pressing with the finger on the stout brass bar *b b* (the section of the bar is $\frac{1}{2}$ in. × $\frac{1}{4}$ in.). This of itself indicates the delicacy of the microphone.

IV. The design of the sending and receiving coils. The author had in each of them 100 turns of insulated copper wire (16 S.W.G.), radius about half a metre, resistance about 3 ohms. If the same wire had been opened out to 50 turns of radius one metre in both sender and receiver, the mutual induction would be four times as great; the self-induction of each would be slightly reduced (roughly to about two-thirds of its former value), but this could be made up in the auxiliary coils. Thus it is advantageous to have the radius of the coils large. In making the auxiliary coils we require to have large L with small R. If we have a given amount of wire at our disposal, it is better to have small radius and many turns, and have a core of iron wires for final adjustment. One advantage of keeping R moderately large in the circuit is that we run no risk of breaking down the condenser in the primary.

V. In Prof. Lodge's research the sound produced at the receiving-telephone was very small, just sufficient for audibility being all that is required by a single observer; but in the case here discussed, we have to produce sounds to be given out to a large audience by a loud-speaking telephone; these would have to be, and were, thousands of times as great as required in the former case. The process of amplifying the small currents until they become large and produce really loud signals is a difficult one in itself; but an even greater one arises from the passage of large currents through the last microphone ; the carbon-contacts are rapidly burnt away, and as a microphone contact is a very delicate one, continual adjustment is required.

To meet this special difficulty Prof. Lodge has employed an ingenious device which should be mentioned. The upper carbon is attached to a large mass which turns freely on a horizontal axis, which is so counterpoised that the two carbons are gently but steadily pressed together. If the carbons burn away at the contact, the pivoted system moves on its axis and maintains the same microphone-action as before. Thus the contact is kept automatically in working order.

It should be pointed out that though the sounds produced in the receiver were much louder than in the case of Prof. Lodge's system, yet the distance between sender and receiver was in his case very much larger; so that each arrangement has its own difficulties.

Another Experiment.

By a small modification in the primary circuit, tuning can be demonstrated in a very striking way. In fig. 1 put a loud-speaking receiver in series with the coils C_1 and C_2, and shunt it by a resistance-box. On working the circuit this receiver gives out a loud sound of the circuit-frequency ; by changes in the shunt we can affect its intensity, while by changes in L or C we alter its frequency. It may be mentioned in passing that this is a convenient means of producing a sound of constant intensity and is easily adjustable (though not necessarily pure), and as such it has been used by the author.

As a simple example, if we change the capacity from 0·9 mfd. to 0·4 mfd., then the frequency should change in the ratio $\sqrt{\frac{4}{9}}=\frac{2}{3}$; the notes will be found to have about a musical interval of one-fifth.

The author's best thanks are due to Prof. Lodge for advice during the progress of the work.

Discussion.

Mr. Watson described some experiments which he had shown to illustrate syntony, both by obtaining galvanometer deflexions and sparks in the secondary circuit.

Dr. Lehfeldt asked how the circuit was tuned when it contained both a variable capacity and a variable self-induction.

Mr. Shaw said that the values of the capacity and self-induction were connected with the vibration-frequency by a formula given by Dr. Lodge. Starting with a known capacity, the necessary self-induction was calculated and small alterations produced by means of an iron core.

XXI. *On the Want of Uniformity in the Action of Copper-Zinc Alloys on Nitric Acid.* *By* Dr. J. H. Gladstone, *F.R.S.**

Much attention is being directed at the present time to methods by which it may be possible to determine the heat evolved in the formation of alloys. Among these methods is that of the dissolution of filings of the alloys of copper and zinc in nitric acid, as compared with the dissolution of mixtures of the two metals in the same proportion. This method has been objected to by more than one chemist on the ground that there is no assurance that the same substances, and in the same relative proportions, are produced in each case. As my name appears on the British Association Committee which has adopted this method, I have felt myself under an obligation to make some direct experiments on the point.

In the Report of this Committee, "On the Heat of Combination of Metals in the Formation of Alloys," read at the

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* Read May 11, 1900.

Dover Meeting of the British Association (Report, 1899, p. 246) a table is given containing details of a long series of observations, which show the heat developed during the action of nitric acid on copper and zinc in various proportions, both when the metals are mixed together and when they are in combination as alloys. The difference of heat between the solutions compared has been regarded as a measure of the heat evolved by the combination of the metals in forming the alloy.

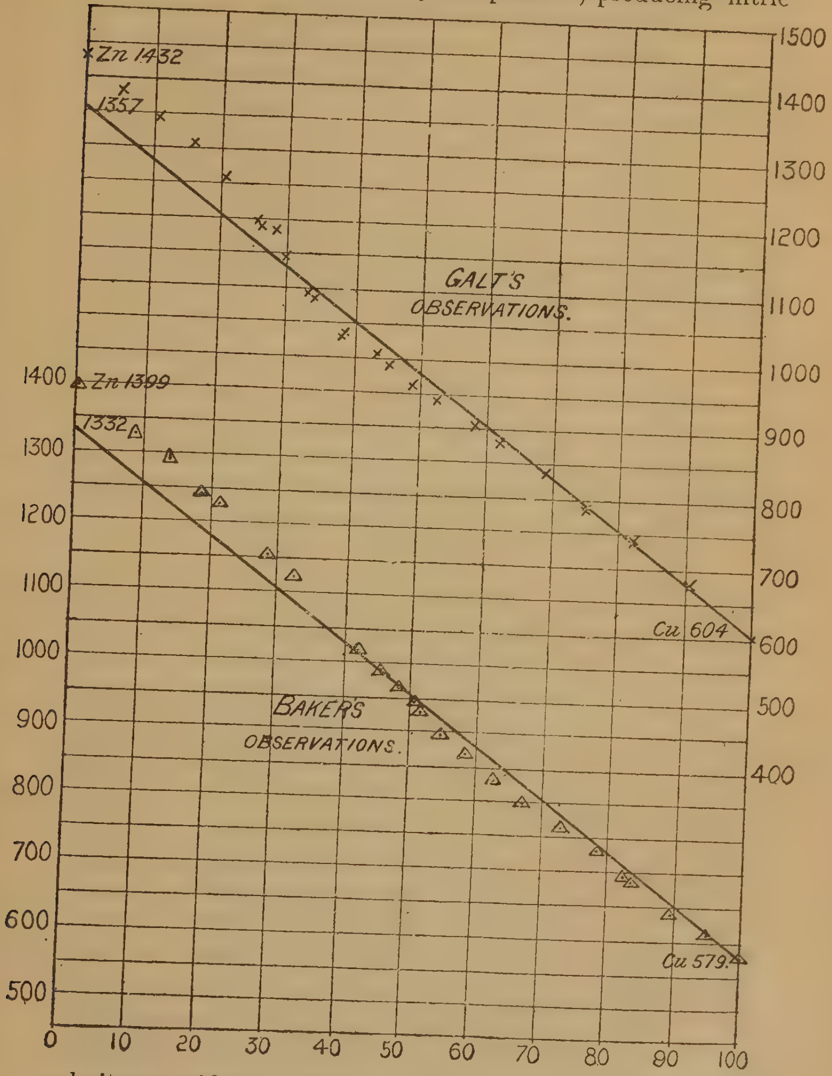
The alloys experimented upon by Dr. Galt are twenty-two in number. The results are set out in a table, and plotted in a diagram. This is reproduced, as far as the little crosses are concerned, on a larger scale in the accompanying diagram.

The crosses represent the absolute amount of heat evolved in dissolving one gramme of metal or alloy expressed in calories. They show at first a pretty regular decrease in the calories from the 1432 evolved by pure zinc towards the 604 evolved by pure copper. But after the alloy containing 20 per cent. of copper, a more rapid and irregular decrease takes place till we arrive at that containing 38 per cent. of copper. From this point, or rather from copper 38·38 per cent., there is a gradual and fairly regular descent to the amount of heat evolved by pure copper.

The somewhat similar series of experiments conducted by Mr. Baker (Proc. Chem. Soc., Sept. 1899) is exhibited in the lower part of the same diagram, the resulting calories being plotted in the same way from 1399 down to 579. There is a fairly close resemblance between the two series, except that in the latter the most rapid decrease of heat does not take place till at about 54 per cent. of copper.

Through the kindness of Lord Kelvin I obtained three specimens of the alloys employed in Dr. Galt's experiments; the first containing 20·5 per cent. of copper and 79·5 per cent. of zinc, the second 38·38 per cent. of copper and 61·62 per cent. of zinc, and the third 49·1 per cent. of copper and 50·9 per cent. of zinc. The first and second specimens are not far from those which show the greatest divergence in opposite directions in the amount of heat evolved; in the third the two metals are very nearly in atomic proportions. In dissolving these in nitric acid I followed essentially the process employed by Dr. Galt, with the precautions mentioned by him.

As is well known, the reaction between nitric acid and these metals or alloys is very complicated, producing nitric



and nitrous oxides and nitrogen, evolved as gases but which may be partially or wholly absorbed; while the liquid is found to contain, in addition to the undecomposed acid, nitrous acid, and nitrates or nitrites of the metals, and in some cases ammonium salts.

The gases have already been the subject of examination by several experimenters. Messrs. Acworth and Armstrong (Journ. Chem. Soc. 1877, p. 54) showed that in the case of copper in nitric acid the gas obtained is almost entirely nitric oxide, while in the case of zinc it is mainly a mixture of nitric and nitrous oxides in very nearly equal proportions. In an experiment with brass they obtained practically the same result as with copper alone. As far then as the gases are concerned, the chemical action of copper and of zinc on nitric acid is not the same; and the insignificant quantity of the nitrous oxide when brass is dissolved suggests an essential difference in the reaction between the alloy and the mixed metals.

It did not seem necessary to repeat the experiments of Armstrong, especially as the permanent gases evolved in Dr. Galt's experiments were small in quantity, at any rate in the case of the yellow alloy. My attention has therefore been mainly confined to determining the substances remaining in solution, *i. e.* the nitrous acid and the ammonia.

TABLE I.

Products of Reaction, calculated for 1 gramme.			
Substance.		Nitrous acid.	Ammonia.
Zinc		0·057	0·0164
Cu 20·5 per cent., Zn 79·5 per cent.:	mixture…	0·165	0·0275
	alloy ……	0·185	0·0098
Cu 38·38 per cent., Zn 61·62 per cent.:	mixture…	0·270	0·0192
	alloy ……	0·552	trace
Cu 49·1 per cent., Zn 50·9 per cent.:	mixture…	0·431	0·0130
	alloy ……	0·568	trace
Cu 65·8 per cent., Zn 33·5 per cent.:	alloy ……	0·568	trace
Cu 73·5 per cent., Zn 26·5 per cent.:	alloy ……	0·600	trace
Copper		0·605	trace

The above Table gives the results; they represent in each case the amount produced by one gramme of metal, mixture, or alloy, as the case may be. Usually 0·4 gramme was dissolved in nitric acid, and the resulting solution was divided into two equal parts for determining the nitrous acid and ammonia respectively. The figures given in the Table are the mean of several observations, which were generally fairly accordant, calculated for one gramme. To these are added the results of two specimens of commercial brass of higher percentage of copper.

If the copper and zinc in the proportions above mentioned had been dissolved separately in acid, and their solutions then mixed together, nitrous acid and ammonia might have been expected to be in the following proportion :—

Table II.

Mixture of Solutions.	Nitrous acid.	Ammonia.
Cu 20·5 per cent., Zn 79·5 per cent.	0·169	0·0130
Cu 33·38 per cent., Zn 61·62 per cent.	0·267	0 0101
Cu 49·1 per cent., Zn 50·9 per cent.	0·326	0·0083

Two results stand out prominently from the above figures.

1. The chemical action of the alloys is very different from the chemical action of the corresponding mixtures of filings. It will be seen by a glance at Table I. that the alloys give much more nitrous acid and very much less ammonia than the corresponding mixtures. In fact, two of these alloys give practically no ammonia.

2. On comparing the figures for the mixtures of solutions in Table II. with the solutions of mixed metals in Table I., it will be seen that there is a notable difference both in regard to the nitrous acid and to the ammonia. This might be anticipated from the fact that, when the copper and zinc filings are mixed together, they form what has been described under the name of the "copper-zinc couple." The two metals in juxtaposition and touching at a multitude of points while surrounded by acid set up a more vigorous action, with

different chemical results and no doubt a different evolution of heat*. It is probably this action which causes Dr. Galt's numbers for heat of mixtures to lie generally below the theoretical straight line joining zinc and copper in the diagram accompanying the report of the Committee.

The chemical objection therefore is well founded. It is a very serious one; but is it necessarily fatal?

Would it not be possible to take some particular alloy, determine the products of its action on nitric acid, and their relative proportions, and then determine the number of calories which would be produced theoretically in the reaction? If they agree closely with the number of calories found by Dr. Galt and Mr. Baker, there is no room for supposing that the amount of heat evolved in making the alloy is to be determined by this method. If, however, the two calculations differ, there is a residual phenomenon to be explained.

But here we encounter two difficulties.

1. Though we may know the ultimate composition of all the specimens of copper-zinc alloys experimented upon, probably not one of them is a truly definite compound. Each of them may consist of two or more alloys with some uncombined zinc or copper, as the case may be. A microscopical examination is generally sufficient to show that each is more or less heterogeneous in its character. Sir W. Roberts-Austen's table of the freezing-points of alloys of copper and zinc also indicates the mixed nature of almost every specimen examined. The alloy Cu 38·38 per cent. appears, however, to be pretty uniform.

2. Supposing, however, that we had the true constitution of the specimen and the exact products of the chemical action both in solution and as gases, there would still remain an uncertainty about the number of calculated calories. The original determinations of Thomsen and the recent ones published by

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* See Journal Chem. Soc., April 1878, where the experiments of Prof. Thorpe and of Gladstone and Tribe on the production of nitrite and ammonia by means of the copper-zinc couple are described.

Berthelot are very discrepant; and the various corrections to be made, especially in regard to the gases, are too uncertain to admit of any trustworthy comparison within the narrow numerical limits with which we have to deal.

There is, however, another method of comparison which appears to be more promising. Although Thomsen and Berthelot differ as to the calories produced by any particular reaction, there is one point on which they practically agree; that is, the excess of calories in a zinc reaction over those in the corresponding copper reaction. Thomsen makes it for one gramme 750 calories, Berthelot 756 calories, which is a practical agreement (say 753 calories). Starting from 604 calories, the value, according to Galt, when pure copper is dissolved in nitric acid of sp. gr. 1·360, we should have 1357 calories when pure zinc is dissolved, *provided the chemical action were the same in each case*; and all the calorimetrical results from the different specimens of alloy would theoretically lie, not upon the line drawn in Dr. Galt's diagram, but upon the straight line drawn between 604 and 1357. On referring to the diagram, we see that the little crosses fairly coincide with this line from pure copper to about the Cu 70 alloy, but beyond that there is less heat produced than the mean indicated by the straight line, the maximum deviation being at about Cu 37. Beyond that point the heat gradually augments, exceeding the mean at about Cu 30, with a somewhat irregular progress to 1432 calories, the amount experimentally obtained by Galt from pure zinc, —an excess of as much as 75 calories above the theoretical. The diagram of Baker's experiments shows the same general result, with the difference previously referred to.

Reference to Table I. will show that the products of decomposition of the nitric acid between pure copper and the Cu 38·38 per cent. alloy give nearly the same amount of nitrous acid in each case (representing about 80 per cent. of the possible amount), and practically no ammonia. The remaining 20 per cent., or thereabouts, consists mainly of nitric oxide. As the products in each of the five cases seem to be the same, and nearly in the same proportions, we should expect that the amounts of heat evolved would form a pretty regular progression between copper and the above alloy, following closely the theoretical line. We see a fair approximation to this in the diagram, but there is a gradual divergence from the line, indicating a deficit of heat. The specimen containing 38 38 per cent. of copper, which is not far from the predominant alloy $CuZn_2$, shows a loss of 32 calories. Baker's experiments show almost exactly the same amount of loss of heat, though at a somewhat different place in the series.

The only way in which, as far as I can see, this residual deficit can be explained on chemical grounds, is by supposing that the action of this alloy upon nitric acid produces a larger amount of nitric oxide than in the case of pure copper. Table I. gives some indication that this may be the case, because the amount of nitrous acid produced is rather smaller in the alloys than with the metal itself, indicating that there must be more of some other product, presumably nitric oxide. But, allowing full force to this argument, it cannot account for as much as 10 calories of the deficit. There is in any case a residual deficit as yet unaccounted for on chemical grounds, and which may be regarded as the amount of heat evolved in the formation of the alloy.

The action of zinc, or of the alloys rich in zinc, upon nitric acid is very different. There is less nitrous acid formed, while ammonia and nitrous oxide are produced in considerable quantities. The substitution of ammonia for nitrous acid will not make much thermal difference; but as the calories obtained by the formation of nitrous oxide are at least 175 more than with nitric oxide, and 83 more than with nitrous acid, there does not seem any difficulty in accounting for the excess shown between the observed and calculated values for pure zinc, or for the alloys containing more than 70 per cent. of this metal.

The work both of Dr. Galt and Mr. Baker has evidently been carried out with the greatest care; but, considering the uncertainty of the thermo-chemical data and the great physical interest attaching to the research, it would seem highly desirable that further experiments on the copper-zinc alloys should be made with solvents which give a chemical action far more simple than that produced by nitric acid.

In concluding, I desire to acknowledge the great assistance Mr. Hibbert has rendered me in this inquiry.

Discussion.

Prof. Armstrong said that the action of nitric acid on brass or zinc and copper was a function of the quantity of acid present, its strength, the temperature, and the pressure, and that therefore it was unsatisfactory to conduct experiments using nitric acid as a solvent. He suggested the use of a solution of bromine, in which finely powdered zinc, copper, and brass are easily soluble with a simple chemical reaction.

XXII. *Notes on the Measurement of some Standard Resistances.*

By R. T. Glazebrook, *M.A.*, *F.R.S.*, *Director of the National Physical Laboratory*[*].

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The problem of comparing together two nearly equal resistance-coils is a much simpler one than that of determining the resistance of a coil of 10, 100, or 1000 ohms in terms of the unit coils. There are various methods by which such comparisons may be made. I had occasion some little time back to determine the resistance of certain coils of 10, 100, and 1000 ohms. I made each determination purposely by two or more methods; and it may be useful to put the results on record with a view of indicating the accuracy which can be reached without any very elaborate precautions. The coils in question were all of platinum-silver with a temperature-coefficient of about ·00028 per 1° C.; and by far the most important source of error is the uncertainty of the temperature.

The 10-ohm coils were measured in three different ways. The first (Method I.) was that employed in constructing the standards of the British Association, and is described in the Report of the B. A. Committee for 1883.

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[*] Read May 25, 1900.

Three 3-ohm coils are wound on the same bobbin. The bobbin is enclosed in a box one face of which is of ebonite through which the six electrodes of stout copper rod project. By means of an arrangement of mercury cups these three coils can be placed in series or in multiple arc. I have acquired the habit of calling this box with its projecting legs the Beetle, and denoting its resistance when in multiple arc by the letter B.

Let the resistances of the three coils be $3+\alpha$, $3+\beta$, and $3+\gamma$ respectively. Then

$$\frac{1}{\mathrm{B}}=\frac{1}{3+\alpha}+\frac{1}{3+\beta}+\frac{1}{3+\gamma}$$

$$=1-\frac{1}{9}(\alpha+\beta+\gamma)+\frac{1}{27}(\alpha^2+\beta^2+\gamma^2),$$

omitting higher powers of the small quantities α, β, γ. Hence

$$\mathrm{B}=1+\frac{1}{9}(\alpha+\beta+\gamma)-\frac{2}{81}(\alpha^2+\beta^2+\gamma^2-\alpha\beta-\beta\gamma-\gamma\alpha).$$

Hence if α, β, and γ are nearly equal, the third term is very small, and we have very approximately

$$\mathrm{B}=1+\frac{1}{9}(\alpha+\beta+\gamma).$$

Now it is comparatively easy to adjust the three 3-ohm coils to equality, and an accurate 3-ohm standard is not required.

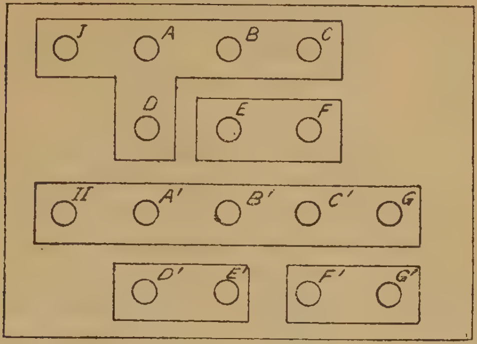
Hence, if B′ be the resistance of the combination when all the coils are in series, then

$$\mathrm{B}'=3+\alpha+3+\beta+3+\gamma=9\mathrm{B}.$$

Or the resistance of the arrangement in series is very approximately 9 times that when in multiple arc.

The arrangement of mercury cups is shown in fig. 1. A number of holes about ·75 centim. diameter are bored through a sheet of ebonite. Thick strips of copper of the form shown in the figure are cemented to the under side of the ebonite, the surface of the copper in contact with the ebonite being amalgamated, and the cups thus formed contain mercury.

Fig. 1.



In the multiple-arc position the 3-ohm coils are connected with AA′, BB′, CC′ respectively; in the series position they connect DD′, EE′, FF′, while a coil of 1 ohm is placed across GG′. The cups I., II. serve to connect the system to the bridge.

Let the resistance of the short rods used for this purpose be U, and the resistance of the 10-ohm coil whose value is required be X.

The first operation is to compare by Carey-Foster's method the Beetle in the multiple-arc position and a standard 1-ohm coil S; let x_1 be the shift on the bridge-wire.

Then we have

$$B+U=S+x_1,$$

or

$$B=S+x_1-U.$$

Next S is placed across the gap GG′ and the Beetle moved into the series position; the combination is then compared with the 10-ohm coil; let x_2 be the shift. Then

$$X=9B+U+S+x_2,$$

$$=10S-8U+9x_1+x_2.$$

So that if U the resistance of the contact-pieces is known, the value of X is found in terms of S.

The chief source of error arises from the difficulty of maintaining the temperature of the Beetle sufficiently steady during the measurements. The consequences due to this can be reduced by taking a series of measurements in order, first with the Beetle in multiple arc, then with it in series. If a given coil be tested by this method at varying temperatures, the observations usually lie on a smooth curve to within about 0°·05 C.

The method was I believe originally devised by Lord Rayleigh in order to construct a coil of 25 ohms from one of 1 ohm. He employed five coils of 5 ohms each; it is the method by which the 10-ohm coils of the Association were constructed.

The other methods employed to determine the 10-ohm coils were both build-up methods. Messrs. Nalder, Bros., kindly put at my disposal a number of boxes arranged as described below.

Each box contained five coils in series and of the values 1, 1, 2, 3, and 4 units. The two ends of the whole series were permanently connected to two mercury cups, and each junction of two consecutive coils was connected to a mercury cup.

Thus the resistance of the series is 10 times that of the first coil.

The coils are enclosed in a wooden box, and are numbered 1 a, 1 b, 2, 3, 4; the unit may be either 1, 10, 100, or 1000 ohms.

The arrangement may be used in two different ways; it is shown diagrammatically in fig. 2.

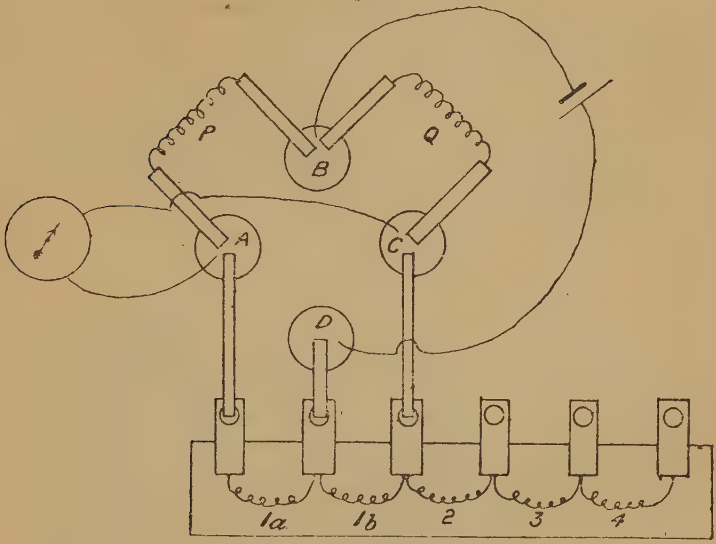
Method II.—Coil 1 a is connected by contact-pieces of known resistance to the Carey-Foster bridge and compared with a known standard S. The value 1 b is found similarly.

Then S is replaced by an ordinary box of coils, and coil 2 of this box is compared with $1\,a + 1\,b$ in series; coil 2 of the build-up contrivance is then compared with coil 2 of the box, and hence with $1\,a + 1\,b$. The comparisons are all done on the Carey-Foster bridge, so that ultimately each coil of the build-up box is known in terms of S and the bridge-wire. Finally, the unknown coil X is compared with $1\,a + 1\,b + 2 + 3 + 4$.

The objection to this method is that it takes some time, and temperature changes lead to difficulty.

Method III.—Although Method II. is applicable to boxes in which the unit is greater than one ohm, it becomes difficult of application unless the wire of the Carey-Foster bridge can be altered. In my bridge the resistance of 1 millim. is ·00005 ohm, and the difference between two coils of 50 or 100 ohms, nominal value, may easily be greater than the whole bridge-wire resistance.

Fig. 2.



It was desirable therefore to devise a method of measuring the resistance of the coils of the box which did not involve the Carey-Foster bridge for the higher resistances.

Two 10-ohm coils P and Q were taken and their difference accurately found on the Carey-Foster bridge; thus, the difference being small, the ratio P/Q is known accurately. The value of the coil 1 *a* is also found on the Carey-Foster bridge.

Four mercury cups, A, B, C, D (fig. 2), are arranged at the corner of a square; the gaps AB, BC contain the coils P, Q respectively. The coil 1 *a* is connected by suitable pieces to A and D, and 1 *b* to D and C respectively.

The resistances of the connecting-rods should be equal.

A battery connects B and D, a galvanometer connects A and C.

If P is equal to Q and 1 *a* to 1 *b*, then there will be a balance; if this is not the case, a balance can be found by shunting P or Q with a resistance W. This resistance need not be accurately known. Thus 1 *b* can be found in terms of 1 *a*. Then 1 *b*+1 *a* can be placed between A and D, and 2 between D and C. Hence 2 can be found and so on. In this manner finally the value of the whole is known.

In the experiments referred to the values of certain standard 10-ohm coils were determined, in all cases by two at least of these methods, with a view to testing the accuracy of the determination. Table I. gives the result.

TABLE I.

Method I.	Method II.	Method III.	Difference expressed as a fraction of the whole.
10·0036	10 0039		−·00003
10·0044	10·0041		+·00003
10 0068		10·0070	−·00002
9·9950		9 9946	+·00004
9·9923		9·9921	+·00002
9·9906		9·9903	+·00003
9·9911		9·9909	+·00002

The first method appears to give slightly higher results than the others, but the differences, with one exception, would be caused by an uncertainty of 0°·1 C., and no attempt was made to read the thermometers to a greater accuracy than this.

In the case of the 100 and 1000-ohm coils Method III. was used; and also a fourth method (Method IV.), that ordinarily employed in testing such coils for the B. A. Committee.

A bridge is formed consisting of the 100-ohm coil to be tested, two 10-ohm coils, and a unit; then by shunting one arm as in Method III., by a resistance which does not require to be accurately known, the value of the 100-ohm coil can be found. In this way the following results were obtained :—

TABLE II.

Method IV.	Method III.	Difference expressed as a fraction of the whole.
100·017 100·020	100·022	– ·00003
100·045 100·047	100·045	+ ·00001
1000·37 1000·36	1000·31	+ ·00005
1000·51 1000·52	1000·50	+ ·00001

In one case only is the difference greater than that due to an error in temperature comparable with 0°·1 C., and it will be noticed that the difference between two determinations of the same coil by Method IV. is comparable with the differences between the results of the two methods.

It thus appears that to an accuracy of some two or three parts in one hundred thousand, the various methods lead to the same results. To reach a higher accuracy would involve, if the coils were of platinum-silver, the knowledge of their temperature to less than 0°·1 C. The end might, however, better be attained by employing manganin or some such alloy.

Possibly this paper may serve a useful purpose by calling attention to the various methods which may be employed to build up multiples of a unit-resistance and by giving some account of the accuracy attained.

A source of uncertainty in resistance measurements is due to the fact that the coils are heated by the current. It is clear that the currents traversing the 1000-ohm coil in the two arrangements described above were different; the concordance of the results tends to show that the error due to heating was in these experiments negligible.

APPENDIX.—*Added Sept.* 18, 1900.

In the theory of Method I. given above, no notice is taken of the fact that the length of copper connecting each of the three 3-ohm coils to the bridge is different. It is easy to do this thus:—Let the resistance between each of the adjacent cups, such as I to A, A to B, B to C &c. be y ohms. Then the resistances of the 3-ohm coils in the multiple arc position are $3+\alpha+2y$, $3+\beta+4y$, and $3+\gamma+6y$ respectively, and neglecting squares of small quantities as before, we have

$$B=1+\tfrac{1}{9}(\alpha+\beta+\gamma+12y).$$

While the series value of the coils is easily seen to be

$$\begin{aligned}B'&=9+\alpha+\beta+\gamma+9y\\&=9B-3y.\end{aligned}$$

The value of y is found by connecting I. and II. to the bridge, short-circuiting the other gap of the bridge and then short-circuiting in turn AA′, BB′, CC′, and finding a series of balance-points. The difference of the readings thus found gives a. In the case of the apparatus used the mean of a number of readings gave

$$a=\cdot 4 \text{ bridge-wire divisions} =\cdot 00002 \text{ ohms}.$$

So that instead of putting $B'=9B$ in reducing the results it would have been more accurate to write $B'=9B-\cdot 00006$. The correction is too small to be of importance. I also found that at a temperature of 16° the value of the 3-ohm coils were respectively 3·0038, 3·0026, and 3·0027.

DISCUSSION.

Mr. CAMPBELL asked if the same degree of accuracy could be obtained with manganin coils; if so, then the small temperature change of manganin would be an advantage.

Mr. TROTTER asked if proper allowance could be made for the large number of mercury cups used in Method I.

Mr. RENNIE advocated the use of the build-up box in preference to the first method. With two mercury cups there is less chance of errors escaping notice than with eight. Every 10- or 100-ohm coil tested at the Board of Trade is subjected to a comparison with a box calibrated by a build-up process.

Dr. HARKER asked if the resistance of the eight mercury cups in series had ever been measured, and, if so, what was the magnitude of the result and what the uncertainty?

Mr. GLAZEBROOK said he had investigated the resistance of the mercury contacts, and it was negligible. In answer to Mr. Campbell, the author said he had no experience of manganin coils himself, but he had seen some figures for German coils which agreed very closely over a considerable period of time.

XXIII. *Note on Crystallization produced in Solid Metals by Pressure. By* W. CAMPBELL.*

[Abstract.]

THE effect of hammering a button of slowly-cooled tin is to produce a fine crystalline structure, the original structure of the tin being almost completely destroyed.

In the preparation of sections of tin, it is found that particles cling to the file and, if allowed to remain, tend to tear the surface of the metal. The effect is not immediately noticeable; but on etching the polished surface there appear besides the usual structure of the tin, lines of much smaller crystals, with irregular boundaries but possessing different orientation. If the tearing effect of the file has been extreme, these crystals may blot out the initial crystallization, produced by the original cooling. If the surface be gradually worn away by continued polishing, these crystals gradually disappear and the usual structure of the tin appears, showing that the effect is only on the surface.

A similar crystallization is set up when a section is cut with a saw. If in the process of polishing the metal thus modified is not cut away, the fine crystalline structure comes out on etching.

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* Read June 8, 1900. (Communicated by Sir W. Roberts Austen.)

Exactly the same effects were produced in case of a copper-tin alloy containing 1 per cent. of copper. Thus it would appear that a metal or even an alloy will rearrange itself under the slight pressure exerted by a file.

Discussion.

Prof. S. P. Thompson suggested that the effect might be due to local heating caused by tearing rather than to pressure.

Mr. Campbell said the effect was not due to the heating of the file, because if the file were kept perfectly clean no crystals formed.

Prof. S. P. Thompson asked if scratching the surface with a diamond produced crystallization.

The Author said he had tried with a sharp knife without success, but cutting with a blunt chisel produced crystallization along the chisel-mark.

XXIV. *An Application of the Method of Striæ to the Illumination of Objects under the Microscope. By* Prof. R. W. Wood *.

[Plate I.]

Having recently made considerable use of Toepler's "Schlieren-Methode," it occurred to me to see to what extent this most sensitive means of rendering visible minute differences in refractive index could be applied to the illumination of objects under the microscope. The deflexion of a long ray of light by the striæ in the object to be observed, being the fundamental principle of the method, it seemed at first sight quite hopeless to get results in the short space between the microscope-objective and the object, and I was much surprised to find how well the method worked, even under these unfavorable conditions. On looking over the 'Beiblätter' of the *Annalen* I found, after finishing my observations, that a similar attempt had been made by W. Seibert, and described in the *Zeitschrift für Instrumentenkunde*, ii. p. 92 (1892). With what success the work was attended I do not know, since, at the present moment, I am unable to get access to the early numbers of this journal.

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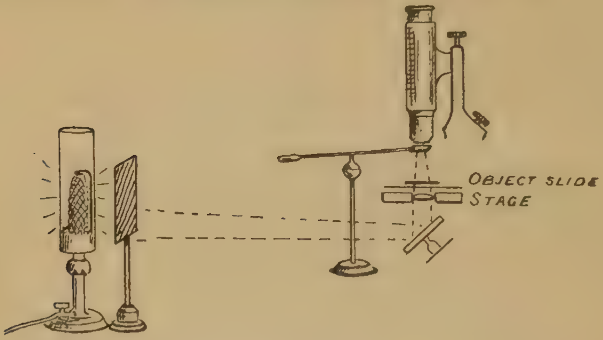
* Read June 8, 1900.

With this preliminary statement I feel warranted in presenting to the Society the results of my observations, as I feel sure that in certain cases the method can be used to advantage in the examination of microscopical objects, in which the detail is lost owing to an almost uniform optical density.

I chose as an object some powdered glass, immersed in cedar oil of the same mean refractive index. The glass particles were almost invisible under ordinary conditions of illumination, as by the use of the substage condenser and diaphragm it was just possible to see the outline of some of the larger particles, but nothing whatever could be seen of their actual form.

I then arranged the illuminating system as follows:—A screen bounded by a straight edge is placed in front of an incandescent gas-lamp, so as to cut off half of the mantle and give a source of light bounded by one perfectly straight side. (A gas-flame with a horizontal screen does about as well.) A small lens of very short focus was placed on the stage, or rather below the stage, as close as possible to the object. The lamp was at a distance of six feet, and the light reflected from the mirror was brought to a focus by this lens, passing through the object on its way. An image of the lamp is formed in space by the lens, and by raising the tube of the microscope the image can be seen. A $\frac{2}{3}$-inch objective was used, the difficulties increasing as we use objectives of shorter focus. A little strip of thin brass, with a carefully-cut straight edge, was fastened to the stand carrying the "bull's-eye" condenser with a bit of wax, and moved into position between the objective and object, so as to cut off the flame-image with the exception of a narrow thread of light along the straight edge. It is important to have the brass screen set *accurately in the plane of the flame-image with its edge parallel to the straight edge of the flame.* This adjustment must be made with the microscope focussed on the flame-image, the brass strip being raised and lowered until it is also in focus. It is then advanced over the flame until nearly all the light is cut off. On lowering the microscope-tube until the object is once more in focus, and carefully advancing the brass strip until practically all of the flame-image is cut off, we shall find that suddenly the glass particles appear with most astonishing sharpness, every irregularity, angle, and facet showing as distinctly as if we were dealing with great lumps of glass in air. The two photographs accompanying this paper (Plate I.) were taken of the same "field" of glass fragments in oil—one with ordinary illumination, the other by the Schlieren-Methode. It is important to choose a lens of such focus that its focal plane shall be half a millimetre or so below the objective when the microscope is focussed on the object. The scheme is shown in the diagram.



While I doubt if this method will be found to have a very wide application, it appears to me that in certain special cases, perhaps in the examination of rock-sections, it may prove useful. From the nature of things it cannot very well be used with high powers, at least it is not so sensitive under such circumstances.

XXV. *A Comparison of Platinum Thermometers of different degrees of Purity.* *By* H. M. TORY, *M.A., Mathematical Lecturer at McGill College, Montreal**.

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1. THIS investigation was undertaken at the suggestion of Professor Callendar with a view to determining the probable order of accuracy in the determination of high temperatures attainable by the use of ordinary commercial specimens of platinum wire. It was also desired to observe the effect of large variations in the purity of the wire, in order to be able to estimate the probable effect of such small impurities as were likely to occur in pure wires specially selected for pyrometry. Five wires in all were compared over the range 400° to 1000° C. The fundamental coefficients of the wires (which may be taken as an indication of the purity) varied from ·003892 to ·002340, *i. e.* by 40 per cent. of the maximum value. It was found, however, that the extreme variations of the temperatures observed, when calculated on the platinum scale by the formula

$$pt=100(R-R^\circ)/(R'-R^\circ), \quad . \quad . \quad . \quad . \quad (1)$$

in which the letters R, R′, and R° stand for the observed resistance at the temperatures pt, 100°, and 0° C. respectively, did not in any case exceed 9° C. at 1000° C., or were less than one per cent. on the interval at any point of the range of observation, in spite of the large differences in the samples.

When the temperatures were reduced by means of the difference-formula

$$t-pt=dt(t-100)/10{,}000, \quad . \quad . \quad . \quad . \quad (2)$$

although the agreement was found to be exceedingly close at temperatures up to 500° C. (if the value of the difference-coefficient d was calculated by assuming the boiling-point of sulphur (S.B.P.) to be 444°·53 C., by the method proposed by Callendar and Griffiths), the discrepancies at 1000° were still of the order of 5° or 10° C. We must conclude that this method of reduction by reference to the

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* Read June 22, 1900.

S.B.P. will not give results of the highest accuracy if applied to impure wires at 1000° C. This point has also been illustrated by Callendar (Phil. Mag. Feb. 1899). It was found, however, that very fair agreement could be obtained at high temperatures by using the freezing-point of silver (AgF.P.) as a secondary fixed point instead of the S.B.P. in the calculation of the difference-coefficient. For two of the wires the simple method of reduction employed by Heycock and Neville (Journ. Chem. Soc. Feb. 1895, and Phil. Mag. Feb. 1899, p. 200) gave results agreeing with the standard wire almost within the limits of error of observation, but did not apply so well in the case of the most impure specimens. It was observed, however, that the differences of the platinum temperatures for all the wires could be very closely represented between the limits of observation by linear formulæ. If the observed values of *pt* for each wire were first reduced to the standard *pt* in each case by the linear relation, and then corrected by the same difference-formula as the standard wire, very consistent results were obtained from all the wires. This method would not be applicable below 400° C., but it might prove a suitable type of formula for purposes of extrapolation, in case it was necessary to employ impure wires.

It is probable that the platinum wires used in this investigation were free from contamination with baser metals outside the platinum group. Under proper conditions they all showed great constancy of zero, and the variation of the difference-coefficients (from 1·50 to 1·67) was comparatively small. By contamination with baser or more volatile metals, it is possible to get much larger variations in the values of *pt* and *d*; but such pyrometers will not show constant results until the volatile constituents have been burnt out. Special attention was given to the effects of annealing which may produce changes of zero of the order of one degree after the first exposure to a temperature of 1000° C. With this exception, no changes of zero of any importance were observed, as the temperatures employed never exceeded 1000° C.

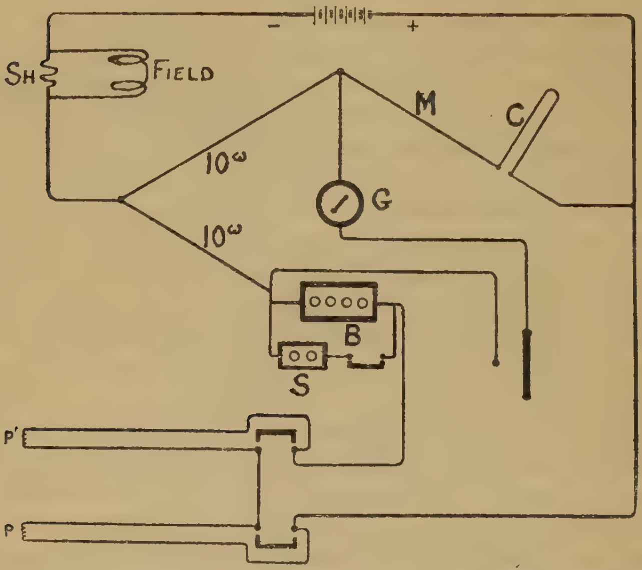
2. *Methods and Apparatus.*—The method of comparison adopted was that described by Callendar (Phil. Trans. A, 1887,

p. 161), in which the wires to be compared are wound side by side in the same tube, so as to be always at the same mean temperature. This method appears to be more accurate than the method of indirect comparison of pyrometers in separate tubes. Observations were taken at steady temperatures only, in a well-stirred bath of melted tin. The apparatus was arranged so that the readings of the two pyrometers were almost simultaneous. Each wire was directly compared with the pure standard wire ; and in addition a specimen of the standard was drawn down to half section, and compared with the original wire. The agreement was found to be exact throughout the scale, as was to be expected with so pure a wire. The wires were wound on mica strips with platinum leads insulated in the usual manner. Each double pyrometer, when completed, had six leads, two each for the pyrometer coils, and two compensating leads. The resistance-box used was one of the type described by Callendar (Phil. Mag. July 1891) with coils on the binary scale, standardized in the usual manner. The contact surfaces of the screw-nuts used for short-circuiting the coils were kept clean, and the contacts frequently tested. The galvanometer used was one specially designed by Prof. Callendar (Phil. Mag. Feb. 1892) for resistance pyrometer work, with an astatic-needle system in which the control is due to the passage of a current through a pair of coils, marked "Field" in fig. 1, at right angles to the position of the galvanometer-coils. The current which effects the control is proportional to that used in measuring the resistance, and hence the deflexion due to any given difference of resistance is constant, no matter what the current may be. It was found, for example, that the deflexion for a difference of resistance of one unit of the bridge, was exactly the same whether a two-volt or four-volt battery was used.

In order to secure a proper sensitiveness of the needle, the field or control coils were shunted with a small resistance marked Sh, which was adjusted so that a change of resistance of one bridge-unit produced a deflexion equal to 10 divisions of the galvanometer-scale. By this means, the deflexions could be read to 1/100 of a degree, which was sufficient for the purpose.

3. *Resistance Measurements.*—The ratio-coils of the bridge were connected permanently in the galvanometer-case, and had a fixed resistance of about 10 ohms each, being made exactly equal. The standard or balancing coil M, against which the resistances of the pyrometer and box were balanced, was also fixed permanently in connexion with the galvanometer, but in such a way that it could be kept in a test-tube of oil, and its temperature taken after each observation. The compensating leads C were in series with this coil. The adjustable resistance-box B was inserted in the same arm as the pyrometer, and readings were taken by the method of substitution, so as to keep the resistance in circuit constant.

Fig. 1.



Before the pyrometer was put in the circuit, the balancing-coil M was adjusted exactly equal to the total resistance of the box B at 20° C., so that when the pyrometer was inserted in the same arm as the box its resistance could be at once determined by reading the resistances of the box that were short-circuited, and taking the deflexion of the galvanometer. In addition to the usual coils in the box, namely, 640, 320, 160, 80, 40, 20, 10 units, two others were added, of 5 and 2 units respectively; so that deflexions of the galvanometer greater than 20 scale-divisions were never required to be taken. Ordinarily it is not necessary to adjust the balancing-coil M equal to the resistance of the box, as only the differences R − R° and R′ − R° are required. It was convenient, however, in order to get the temperature-coefficient of the wire used. The temperature-coefficient of the platinum-silver box coils was determined to be ·000330 per degree, and that of the manganin balancing-coil M to be ·000045. All the observations were corrected for both box and coil.

The resistances of the pyrometers used for comparison, owing to the large differences in the temperature-coefficients of the wires, differed considerably, excepting at the points where they were calculated to agree. The fundamental interval, R′ − R°, was usually calculated for one pyrometer to be 100 approximately, and the other to have a nearly equal resistance at 500°, the temperature-coefficients being roughly determined before the pyrometers were made up. The result of this difference of resistance was, that it was found exceedingly difficult to take readings of the pyrometers in the usual way so quickly as to be sure that the temperature was constant to 1/10 of a degree during the process. The pyrometers were first connected in series, so that one could be immediately short-circuited and the other read after adjusting the resistance in the box. The time required to take a reading in this way, on account of the swing of the needle of the galvanometer, was about three minutes.

4. *Shunt method of Comparison.*—In order to get over this difficulty and secure simultaneous readings, the following method was adopted. The two pyrometers P and P_1 were connected in series with the resistance-box B, through a mercury-cup switch, so that by rocking the top of the switch they could be short-circuited one after the other, by means of thick copper wires attached to the rocker. Connected with the same switch there was an arrangement such that when P_1 was short-circuited and P was to be measured, the box B was shunted by means of a mercury connexion. The shunt-box S was then adjusted so that the deflexion of the galvanometer for P_1 with B unshunted was exactly the same as that of P

with the shunt S in parallel with B. The shunt S was a standard resistance-box in ohms with an attachment for reading to tenths. As the shunt S was usually large compared with B, it was not necessary to know S nearer than 1/10 of an ohm, while the change of resistance, due to the change of temperature of the box, was negligible. Further, an arrangement was made on the same switch for opening and closing the galvanometer circuit, so that the galvanometer was opened first and closed last on rocking the switch. The result was, since, as before stated, the units of the box were so arranged that a deflexion of 20 scale-divisions was the largest necessary, that with a little practice the switch could be rocked and the deflexions of the two pyrometers read almost simultaneously, the needle of the galvanometer not swinging more than a couple of scale-divisions. The readings could be easily taken within five seconds of each other, and verified again and again without the slightest difficulty, as the temperature slowly changed. The use of the shunt, while it diminished the difficulty of taking observations, somewhat increased the labour of calculation. If (P_2-P_1) be the difference of resistance of the two pyrometers for any temperature, and B the resistance in the box which with the pyrometer P_1 balances the standard coil M, and if S be the shunt to B for the second pyrometer P_2, then

$$M=P_1+B=P_2+BS/(B+S),$$

whence

$$P_2-P_1=B^2/(B+S), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

assuming the deflexions of the two pyrometers to be the same. The factor for reducing the units of the shunt-box (ohms) to units of the pyrometer-box was determined from equation (3) by observations taken at 0°, 100°, and 444°·5 (the boiling-point of sulphur) first with the two pyrometers separately using the box B only, and then simultaneously, using the shunt with the second pyrometer.

5. *Method of Heating.*—In order to get an accurate comparison, only steady temperatures were used. For this purpose, the pyrometers, enclosed in a porcelain tube, were heated in an iron pot of molten tin, and the gas-supply regulated by means of a constant-pressure gas-regulator. The gas also flowed through a graduated gas-supply regulator,

so that, with a little patience, almost any temperature between 400° and 1000° C. could be obtained. The furnace used was one whose maximum was 1000°, so that the observations were not taken beyond that point. The molten tin was continuously stirred by means of an air-engine and stirrer. It was found necessary to make the stirrer of fire-clay or tool-steel. When iron was used, the action of the tin at its surface, on the iron, soon rendered it useless. To prevent oxidation of the tin, which took place very rapidly when the surface was exposed, and as a result soon filled the pot with tin oxide in a semi-viscous condition, various expedients were used. The one which succeeded best was to keep the surface covered with a stratum, half a centimetre thick, of ground arc-light carbon.

The greatest difficulty experienced was due to the action of the tin on the porcelain tubes. They would not stand repeated heatings in the tin bath, but became very rotten. Several of the observations were spoiled by the tubes breaking at the moment of removing them from the molten tin. It was sometimes difficult at first to remove the pyrometer-tubes, because of the oxidized tin on the surface. After the difficulty of oxidation was overcome, less trouble was experienced, but the tubes were never used more than two or three times without becoming so affected at the junction with the surface of the tin, as to make it undesirable to use them again. In taking the melting-point of silver, the tubes which had been previously used for only one set of observations in tin, generally broke when removing them from the melted silver, though the greatest care was exercised.

6. *Results of Observations.*—Four different samples of ordinary platinum wire were compared with a very pure specimen in general use in the laboratory as a standard, between 400° C. and 1000° C., the two extremes of the furnace used. The temperature-coefficient of the standard wire was found to be slightly different in different pyrometers. These variations were due doubtless to the lack of absolute uniformity in the wire, but were not sufficiently large to affect the readings of temperatures at 1000° by more than 1/10 of a degree. The difference-coefficient d of each wire in the formula (2) was calculated from an observation of the boiling-point of sulphur in the usual way.

The accompanying curves (fig. 2) show graphically the relations between the various wires, plotted with the platinum temperatures of the standard wire as abscissæ and for ordinates, the differences $Pt'-Pt^{\circ}$, the difference-curve belonging to each wire being denoted by the value of its d. It will be seen that *the difference-curves are all nearly straight*, between the limits of observation. It follows that a linear relation, involving only two unknown quantities, will express the relation of any one of them to the standard, thus:—

$$pt-pt'=a\,pt+b,$$

which may be written, if a is small,

$$pt=pt'+a\,pt'+b. \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

By observing therefore the differences between the platinum temperatures of the wires for two points, such as the S.B.P. and the Ag F.P., the constants in formula (4) can be found for each wire.

Table I.

Values of Constants a and b in the Linear Formula (4), for each of the Impure Wires as compared with the Standard.

No. of Wire.	Difference-Coefficient.	Fundamental Coefficient.	Coefficient a.	Coefficient b.
1	1·595	·003164	+·0103	$-\overset{\circ}{3}\cdot 14$
2	1·670	·002689	+·0124	−2·65
3	1·645	·003216	+·0142	−3·80
4	1·530	·002340	−·0106	+5·73

Since the differences are so small between the different wires, the platinum temperatures observed with each wire can be easily reduced to the scale of the standard wire by the linear formula (4), and then corrected by the standard difference-curve to the scale of the gas-thermometer. The results thus obtained would agree within the limits of the present series of observations with the Standard Scale recently

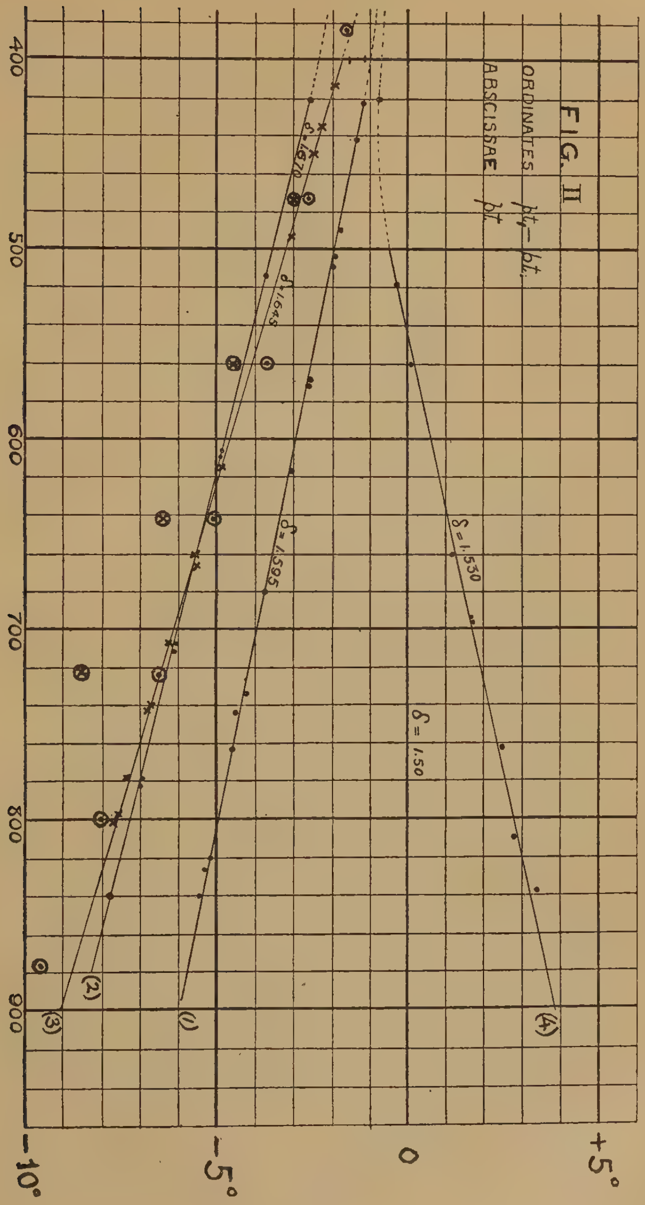


Fig 2.—Differences of Platinum Thermometers from Standard, referred to pt as abscissa. ⊗ Points calculated by Difference Formula for $d = 1·650$. ⊙ Ditto by Heycock and Neville's Method.

proposed by Callendar (Phil. Mag. Dec. 1899), which is based on the application of the difference-formula (2) to the pure standard wire. In this paper, it is pointed out that in all probability the value there given for the melting-point of silver, viz. 960° C., is correct to within 1° or 2°, and it is suggested that a standard platinum wire be adopted, any other wire being referred to it by determining the melting-point of silver or gold, and the boiling-point of sulphur. To the evidence there adduced might be added the redetermination of the melting-points of gold and silver, by M. Berthelot, who gives the two points as 962° C. and 1064° C. It seems to be a reasonable conclusion, therefore, that from 0° up to the melting-point of gold, 1060°, at least, a practical thermometric scale could be established, which would at no point differ from the gas-thermometer scale by more than 2° or 3°. It would follow that all observers working with platinum pyrometers could, in a most certain and ready manner, compare their results. The standard sample would thus be defined as a wire with a definite sulphur boiling-point, and a definite silver melting-point. In fact a number of definite points could be defined up the scale, any two of which could be used.

I have not yet carefully studied the difference below 400° or above 1000°, but hope to do so in the near future. It would appear, however, from results obtained, that the linear difference-curve commences to bend below 400°, meeting the reference line at 100° C. Such a process of reduction is hardly necessary, however, below 500° C., as in any good specimen of platinum wire the temperatures can be reduced directly by the difference-formula, using the value of d determined from the S.B.P.

7. *Variation of Temperature-Coefficients.*—Since the differences between the platinum temperatures of two wires depend on the rate of change of the temperature-coefficients of the wires, the following table may not be uninteresting:—

TABLE II.

Values of Temperature-Coefficients over Different Ranges.

No. of Wire.	Difference Coefficient.		Fundamental Coefficient, c.	Coefficient $0° - 445°$.	Per-cent. of c.	Coefficient $0°-960°$.	Per-cent. of c.
	S.B.P.	AgF.P.					
1	1·595	1·561	·003164	·002991	94·6	·002739	86·6
2	1·670	1·592	·002689	·002533	94·7	·002322	86·4
3	1·645	1·600	·003216	·003033	94·3	·002775	86·3
4	1·530	1·461	·002340	·002215	94·6	·002047	87·4
Standard	1·500	1·500	·003892	·003692	94·8	·003391	87·0

It will be observed that the percentage diminution of the coefficient of each of the wires is nearly the same over the range 0° to 960° in terms of the fundamental coefficient. It follows that the values of the difference-coefficients obtained by reference to the AgF.P. are nearly the same, and afford a convenient method of reduction at temperatures near 1000° C. The S.B.P. difference-coefficients do not give very good agreement at 1000° C. for impure wires.

8. *Method of Heycock and Neville.*—In the simple and convenient method of reduction employed by Heycock and Neville, the difference-coefficients for the various pyrometers are calculated as usual from the S.B.P., but the reduction of the observations from pt to t is effected by means of a single difference-curve, drawn for the standard wire only, in terms of pt as abscissa. The platinum temperature pt observed with any pyrometer is reduced to the normal scale by taking from the standard curve the difference $t-pt$ corresponding to the observed value of pt, and increasing it in the ratio $d/d°$ of the appropriate difference-coefficient d to the standard $d°$. This method does not give absolute agreement with the difference-formula (2) unless $d=d°$, but it often appears to give more consistent results than (2) in the case of impure wires at 1000° C., and it is simpler to apply, as it requires only one difference-curve, which is drawn for the standard wire.

The following tables will show how close this agreement is for three of the wires tested. The first column shows, for each case, the temperatures for the standard wire corrected by the difference-formula; the second, headed Test, shows the corresponding values for the impure wire, corrected by Heycock and Neville's method.

Table III.

Reduction by Heycock and Neville's Method.

Standard.	Test No. (1).	Standard.	Test No. (2).	Standard.	Test No. (3).
948·58	948·66	965·9	968·9	932·5	932·9
937·90	938·16	882·8	884·9	939·6	939·8
864·55	864·55	882·3	884·5	882·7	882·6
839·37	839·10	793·9	795·4	832·4	832·1
821·23	821·24	785·7	787·1	831·8	831·6
753·49	753·51	786·1	787·3	788·6	788·6
673·33	673·22	659·5	660·0	738·7	738·5
621·79	621·72	664·6	664·8	729·0	728·8
619·67	619·61	551·4	551·3	675·9	675·6
550·39	550·32	551·8	551·6	623·2	622·9
549·89	549·81	440·0	443·7	597·5	597·3
522·75	522·88			525·9	525·6
469·78	469·86			479·9	479·7
				434·0	433·9

It will be seen that for the first and third wires the results are in agreement, almost within the limits of error of observation by direct comparison. In the second wire the agreement is not so complete, which is not at all remarkable when it is observed that the temperature-coefficient of this wire is 33 per cent. less than that of the standard. The fourth wire (the most impure) does not agree at all when reduced by this method*.

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* *Footnote added by Prof. Callendar.*—In order to illustrate the nature of the agreement of the observations with the difference-formula and with Heycock and Neville's method, I have inserted in fig. 2 a series of points representing the values of the differences $pt' - pt$ for a wire $d = 1{\cdot}650$ calculated by the two methods, $\oplus$ by the difference-formula, $\odot$ by Heycock and Neville's method. It will be observed that up to 600 pt both methods agree about equally well with the observations. Above 600° the observed difference is much less than that calculated by the difference-formula. The second method agrees very fairly up to 800°, but tends to diverge from the linear formula beyond that point.

9. *Effect of Annealing.*—As before stated, considerable changes of zero were found in some of the wires on first heating them to 1000° for a couple of hours, in one instance a rise of no less than 2°. In this extreme case, there seems to be no reason to doubt that the mica used was largely the cause, as the wire after prolonged use became slightly discoloured. A specimen of the mica used was tested chemically and found to be slightly acid. The standard wire, which was chemically very pure, was also slightly affected in this pyrometer; and hence the observations were disregarded. Afterwards some white mica was obtained, from the Instrument Co., Cambridge, and when proper precautions were taken in winding and annealing, the standard wire never showed changes of zero greater than 0°·2 or of F.I. greater than 0°·03, after heating to 1000° C. Most of the impure wires used, however, showed changes somewhat greater than this. In the case of the wire $d = 1670$, a fall of 1°·2 was observed in the zero *on first annealing* at 1000° for one hour. This was doubtless due to the fact that, in winding the coil, the wire, as bent on the frame, was in a state of unequal tension, and when heated to 1000° this was relieved, with a consequent fall of zero on cooling. For accurate work, too great care cannot be exercised in winding the pyrometer-coil. A fall of zero may be easily produced as above, or, if the wire be wound too tight originally, a thickening of the mica may cause a rise of zero, as suggested by Heycock and Neville. *After the coil is wound*, the pyrometer should be annealed for some time at a temperature beyond that for which it is to be used, and allowed to cool slowly and equally, before the constants are determined. If the pyrometer is used frequently for high temperatures, it is occasionally necessary to redetermine the zero in the most accurate work to allow for minute progressive strains.

10. *Effect of Wire-drawing.*—In order to test the effect of the mechanical working of the wire on its thermometric scale, I had a piece of wire of diameter 6 mils drawn down to 4 mils, and a double pyrometer made from these two. The wire was softened by passing quickly through a bunsen-flame before winding, but not annealed after winding. On

determining the constants, it was found that the platinum temperatures for the boiling-point of sulphur differed by 1°·30. The pyrometer was then heated to 1000° for an hour, and slowly cooled, and the constants again determined. The wires then agreed at the boiling-point of sulphur to ·01 of a degree, and on taking the melting-point of silver a proportionately good agreement was obtained. The difference in the first case was certainly due to insufficient annealing. The pyrometer was tested again and again, and the results were always in complete agreement. These observations on samples of the same wire led to the conclusion that the constants determined *after* the high temperatures and not *before*, as suggested by Heycock and Neville, should be used in the calculations (provided that the wire is not strained in cooling), and this has been uniformly done, but the difference in any case is very slight.

The wires used differed greatly in specific resistance. In all cases, the wires with the smallest temperature-coefficients had the largest specific resistance, and, with the exception of No. 4, gave the lowest platinum temperatures. The wire $d=1\cdot670$ had a specific resistance about 30 per cent. greater than that of the standard, and the others nearly as great, but the measurements of specific resistance could not be made very accurately on wires of so small a diameter.

In conclusion, I must thank Prof. Callendar for kind assistance, Miss Harriet Brooks, B.A., of the Royal Victoria College, and Mr. N. M. Yuile, M.Sc., of the Mining Department, McGill College, for assistance in taking observations.

McGill College, April 19th, 1900.

XXVI. *Notes on Gas-Thermometry.* *By* P. Chappuis, *Ph.D., Savant Attaché au Bureau International des Poids et Mesures, Sèvres, France**.

I. In a recent research, the results of which have just appeared in the Philosophical Transactions of the Royal Society, Dr. J. A. Harker and the author endeavoured to compare the indications of the platinum resistance-thermometer and the normal scale over the range −20° to 600°†.

Having been led to recognize that hydrogen could not be employed as thermometric substance on account of its action on the walls of the glass reservoirs at high temperatures, we had recourse to a constant-volume nitrogen-thermometer having an initial pressure slightly under 800 millim., and assumed provisionally that the thermometric scale of this instrument represents the normal scale of temperature. It is of interest to ascertain whether this hypothesis is justified by the facts, or in other words to determine the divergence of the constant-volume gas-thermometer from the normal scale at high temperatures.

Corrections to the Nitrogen Thermometer.

Measurements previously made with a constant-volume nitrogen-thermometer‡ having an initial pressure of one metre have shown that the cofficient $\frac{1}{P_0}\frac{dP}{dt}$ varies to an appreciable extent, so that under these conditions the divergence between the nitrogen thermometer and the normal scale attains 0·01 at its maximum near 40°.

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* Read June 22, 1900. Translated from the Author's MS. by J. A. Harker.

† The temperature scale adopted as the standard by the International Committee of Weights and Measures is defined as the Centigrade Scale of the Hydrogen Thermometer, having as fixed points the temperature of melting ice (0°), and that of the vapour of distilled water in ebullition (100°) under the normal atmospheric pressure; the hydrogen being taken under the manometric initial pressure of one metre of mercury, *i. e.* at $\frac{1000}{760}=1{\cdot}3158$ of the atmospheric pressure.

‡ Chappuis, *Travaux et Mém. du Bureau International*, vol. vi. 1888.

The expression for the dilatation of nitrogen at the temperature t° deduced from the observations made with this thermometer is

$$0{\cdot}003\,676\,98 - 7{\cdot}826\,746 \times 10^{-8} t + 4{\cdot}780\,076 \times 10^{-10} t^2.$$

The values deduced from this function for a few points are

Temp.	Coeff.
0°	0·00367 698
20	560
40	461
50	427
60	400
70	384
80	378
90	381
100	0·00367 393

From this expression it appears that the coefficient of dilatation of nitrogen diminishes gradually up to about 80°, then increases very slightly. This increase, which is of the same order of magnitude as the probable errors, is not in agreement with our knowledge of the variations of the coefficients of gases. It is very probable that the coefficient approaches a definite limiting value for each initial pressure, which in this case seems to be attained below 100°. In fact, nitrogen at 100° behaves like hydrogen at the ordinary temperature, its compressibility being less than is required by the Boyle-Mariotte law. It may be seen from the table just given that this limiting value of the coefficient is approximately

$$\alpha_2 = 0{\cdot}00367\,380.$$

Assuming this value, it is possible to calculate the fictitious initial pressure which should have been observed if the nitrogen had retained down to 0° the properties of a perfect gas.

We thus obtain the following relations:

$$P_t = P_0(1 + \alpha t)\ ; \quad \text{whence } P_0 = \frac{P_t}{1 + \alpha t}.$$

But from direct observation we have

$$P_0 = \overset{\text{Metre}}{1}, \text{ and } P_{100} = \overset{\text{Metre}}{1{\cdot}367466},$$

whence we obtain for the mean coefficient of dilatation α_1 between 0° and 100°

$$\alpha_1 = 0{\cdot}003674\ 66.$$

The fictitious initial pressure of the nitrogen thermometer supposed perfect may be deduced from the expression above :

$$p_0 = \frac{P_{100}}{1 + 0{\cdot}00367380 \times 100} = \overset{\text{m.}}{1{\cdot}000063}.$$

From these data it is a simple matter to calculate the divergences of the nitrogen thermometer from the normal scale within the interval covered by our comparisons.

Temperature.	Differences of Scale. Actual Scale—Normal Scale. $P_0 = 1$ metre.
100°	0·000
150	−0·008
200	−0·017
250	−0·026
300	−0·034
350	−0·043
400	−0·051
450	−0·060
500	−0·068

From this it would appear that the pressures indicated by a constant-volume nitrogen-thermometer are a little too low, but the errors are small and appear to be of less account than other sources of uncertainty which enter into the measurements. Besides I would remark that in our comparisons of the platinum-thermometer with the nitrogen-thermometer, the initial pressure was always less than one metre. (In the comparisons between 100° and 200° it was 793 millim , and in those between 250° and 500° it was always less than 550 millim.) Under these conditions the systematic divergences of the nitrogen scale from the normal are probably diminished in the same proportion as the initial pressures. They will then be less than 0°·01 for measurements at temperatures near the boiling-point of sulphur.

II. *Determination of the Sulphur-Point.*

The mean result of our experiments for the determination of this important point is

$$T_s = 445^{\circ}{\cdot}2$$

under the barometric pressure of 760 millim. Messrs. Callendar and Griffiths, employing the constant-pressure air-thermometer, have found for the same point

$$T_s = 444^{\circ}\ 53.$$

The difference between these two results—0° 7— is, I believe, to be attributed to the joint action of several causes :—

(1) The scale of the constant-pressure nitrogen-thermometer diverges more widely from the normal temperature-scale than that of the constant-volume thermometer. From experiments made at the Bureau International in 1888*, it would appear that the divergences of the former are about double the latter. Reduction to the normal scale would raise the result of Messrs. Callendar and Griffiths at least a tenth of a degree.

(2) The coefficient of expansion of air at constant pressure, determined by Messrs. Callendar and Griffiths and used by them in the determination of their temperatures, is

$$\alpha = 0{\cdot}003\ 6749.$$

This coefficient is very sensibly greater than that obtained for air under similar conditions of pressure by Regnault, who found

$$\alpha = 0{\cdot}003\ 6700\ ;$$

or the result given by my own more recent experiments,

$$\alpha = 0{\cdot}003\ 6708.$$

If in the calculation of Callendar and Griffiths's experiments they had taken the latter value,

$$\alpha = 0{\cdot}003\ 6708,$$

their value for the boiling-point of sulphur would become 445°·0 instead of 444°·53.

(3) A possible cause of part of the divergence may also be

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* *Proces-verbaux des séances de* 1888, p. 98 *et seq.*

sought in one of the elements entering into one of the corrections involved in the determination of temperatures with the gas-thermometer, namely, the dilatation of the material of the reservoir, discussed at some length by Prof. Callendar in a recent article in this magazine, vol. xlviii. p. 542.

It is customary to express this dilatation by a function of the form

$$v_t = v_0(1 + \alpha t + \beta t^2),$$

in which α and β are constants.

The determination of the constant α is of no great importance in the measurement of temperatures by the gas-thermometer.

The value of α only affects the value obtained for the coefficient of the dilatation of the gas, It is, however, otherwise with the coefficient β, the influence of which increases with increase of temperature. (See in this connexion, Callendar, *loc. cit.* p. 544.)

Of the methods actually employed for the determination of coefficients of expansion, the most precise is undoubtedly that of Fizeau. But up to the present no experiments have been made by this method above 100°.

It follows that coefficients deduced from experiments made with this apparatus are only rigorously applicable over the range 0°–100°*; and it may justly be objected that extrapolation to 450° might introduce into the results quite sensible errors. The dilatation of Berlin porcelain, which is the material out of which the reservoirs employed for the higher temperature work were made, was determined by me over the interval 0°–100°. I found for the cubical dilatation

$$v_t = v_0(1 + 8{\cdot}0703 \times 10^{-6}t + 8{\cdot}98 \times 10^{-9}t^2).$$

The importance of the second term is easily seen. It is sufficient to note here that if, instead of this expression, we take

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* The fundamental study of the dilatation of the three screws of the platinum-iridium tripod, which constitute the standard to which all measurements with this apparatus are referred, was made with great care by M. Benoit, the Director of the Bureau International, and is described in full in the *Trav. et Mém* t. vi., 1888. This laborious piece of work, which is attended with peculiar difficulties, would have to be extended to higher temperatures, if it were desired to extend upwards the range over which the Fizeau apparatus can be employed.

$$v_t = v_0(1 + 8{\cdot}96835 \times 10^{-6}t)$$

(which is the mean coefficient between 0° and 100°), we should have for the sulphur boiling-point

$$T_s = 444{\cdot}3$$

instead of the value 445·2, which results from our calculation.

Mr. Bedford has recently published in these Proceedings * the results of a determination of the dilatation of a tube of Bayeux porcelain, obtained by a method previously employed by Callendar and Griffiths.

The porcelain tube, which served for Mr. Bedford's measurements, had external and internal diameters of 17 mm. and 10 mm. respectively. Near the ends were two marks, 91·4 cm. apart, made by a diamond. The variations in the distance apart of these two marks were measured by a comparator provided with two microscopes under which could be brought successively the porcelain tube and a glass tube maintained at constant temperature.

The porcelain tube could be heated to any temperature between 0° and 840°, which was measured by the change of resistance of a platinum wire traversing the whole length of the tube and furnished with Callendar's compensating leads.

The observations, which are given in detail in the paper, led Mr. Bedford to the following expression for the cubical dilatation of Bayeux porcelain:—

$$v_t = v_0(1 + (10275t + 3{\cdot}24t^2)10^{-9}).$$

Treating the same observations by least squares, I found the slightly different result

$$v_t = v_0(1 + (9715{\cdot}6t + 4{\cdot}43t^2)10^{-9}).$$

Or, if the temperatures thus found on Callendar's scale are reduced to the new scale on which our experiments are calculated :—

$$v_t = v_0(1 + (9781{\cdot}4t + 4{\cdot}276t^2)10^{-9}).$$

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* *Ante*, p. 148.

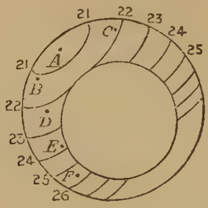
The incontestable advantage of the method employed by Mr. Bedford is that it allows the determination of the dilatation over the same temperature range as the thermometer reservoir is subsequently to be employed; but nevertheless the fact cannot be ignored that to obtain very exact results by a process of this kind must be a matter of extreme difficulty.

I would first remark that the marks made on the tube are more than 8 millim. distant from the neutral plane; and under these conditions the mode of support of the tube must necessarily exercise a considerable influence on the results obtained. And, further, apart altogether from the inevitable variations in the distance between the supports, produced by the expansion of the medium in which they rest, we have the possibility of sensible variations in the elastic constants of porcelain, as yet undetermined at high temperatures.

From the author's indications it would seem that during the experiments the porcelain tube suffered a perceptible change of form. Further, the homogeneity of tubes of this kind is often somewhat doubtful, particularly when, like Mr. Bedford's, they are glazed. I have the advantage of possessing a specimen of Mr. Bedford's tube, obtained by the kindness of Prof. Callendar. The hole through it is considerably eccentric, so that opposite parts of the wall present variations in thickness of from 2 to 4 millim. The glaze having a coefficient of expansion probably differing slightly from that of the mass, it seems quite possible that the tube might become slightly deformed on heating. In that case, once the scratches on it are not strictly in the plane of the neutral fibres, every variation in the curvature of the tube involves a change in the distance apart of the marks.

Under these conditions it would appear to me that Mr. Bedford's results, in spite of their real value, should not be accepted without reserve; and consequently I cannot wholly accept the conclusions of Prof. Callendar, who, after having compared the coefficients determined by me between 0° and 100° for "verre dur" and porcelain with those obtained by the method just described, is of opinion that my values of β are too large.

Bayeux porcelain having probably a composition differing slightly from that of Berlin, I thought it worth while to make a determination in the Fizeau apparatus on the specimen of Mr. Bedford's tube, which I had obtained. The specimen as prepared had a length of about 15 mm. The upper and lower plane surfaces were polished, and were very nearly perpendicular to the axis of the tube. The accompanying figure represents the aspect of the fringes * of sodium light on this specimen in the first experiment made at 83°·3. At each steady temperature an estimate was made of the positions of each of the points A, B, C, D, E, F marked on the lens with reference to the fringes, which were numbered from the centre of the system outwards.



The irregularity of section of the tube and the defects in the surface as ground and polished, have rendered it impossible to operate on a larger number of points of reference.

The set comprising 33 separate observations, spaced out over the interval 1° to 83° gave for the linear dilatation of porcelain

$$l_t = l_0(1 + (2824{\cdot}1t + 6{\cdot}17t^2)10^{-9}),$$

and for the cubic dilatation,

$$V_t = V_0(1 + (8472{\cdot}4t + 18{\cdot}53t^2)10^{-9}).$$

On comparing this result with that obtained by Mr. Bedford, it will be seen that the coefficient of the term in t^2 is here about four times as great. It is also about twice as great as that obtained formerly for Berlin porcelain $(8{\cdot}98 \times 10^{-9})$.

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* In the memoirs of M. Benoit on the Fizeau apparatus published in *Trav. et Mém.* tom. i. & vi., will be found all details regarding the measurement of dilatations by this ingenious method.

If we recalculate the last experiments made by the Fizeau apparatus, assuming the values of the coefficients as found by Mr. Bedford, we obtain the following numbers, alongside of which I have placed the values deduced from my observations:—

T.	Calculated from Bedford's Experiments. Fringes.	Observed.	Obs.—Calc.
20°…………	5·07	5·42	+0·35
40°…………	10·56	11·07	+0·51
60°…………	16·07	16·53	+0·46
80° ………	21·58	21·82	+0·24

The divergences Obs.—Calc. are so large as to be quite inexplicable by errors of observation, since in my experiments the largest residual errors are very rarely as much as a tenth of a fringe. It would appear, then, that there is an incompatibility between the two results, at least over the range of temperature covered by both. But the measurements on the Fizeau apparatus have revealed a fact, which I have mentioned already and which, I think, is likely to be the principal cause of the difference between us. On summarizing in tabular form the displacements of the fringes, as measured with regard to the different points of reference, it is evident at once that the thick part of the tube expands more than the thinner part.

If the dilatation of the tube were uniform over its whole cross-section, the differences between the readings obtained for the different points should be the same at all temperatures. But if, in this case, we take for two widely differing temperatures the differences from the mean for the six points mentioned, we find values which are by no means identical. The following example relates to the two series of observations at 82° and 3° respectively :—

Difference of the individual estimations from the means M_1 and M_2.

Group at 82°.		Group at 3°.		Difference.
	$\frac{\lambda}{2}$.		$\frac{\lambda}{2}$.	$\frac{\lambda}{2}$.
A–M_1	−1·89	A–M_2	−1·72	−0·17
B–M_1	−1·53	B–M_2	−1·47	−0·06
C–M_1	−0·61	C–M_2	−0·52	−0·09
D–M_1	−0·35	D–M_2	−0·39	+0·04
E–M_1	+1·30	E–M_2	+1·20	+0·10
F–M_1	+3·10	F–M_2	+2·92	+0·18
M_1=22·62		M_2=0·59		

The observations made at intermediate temperatures confirm the rotation of the fringes indicated by the two series just quoted; and since, in the course of the observations, the direction of the temperature-change was varied frequently, the fact just mentioned seems well established.

The inequality in the dilatation of the two opposite sides of the tube necessarily involves a change in its form. The tube curves on expansion, which is probably the cause of the divergence found between Mr. Bedford's results and mine.

The conclusions of the study made by Dr. Harker and myself of the thermometric scale of the platinum-resistance thermometer and the sulphur-point do not appear to me to be invalidated by the results collected by Prof. Callendar, and I think we are justified in adhering to them, whilst recognizing at the same time the uncertainty which attaches to an application of the coefficient of expansion of the reservoir over an interval about four times as great as that in which it was determined, and where alone it is strictly applicable.

Consequences of a Change in the Sulphur-Point.

The modifications resulting in the adoption of our new value for the boiling-point of sulphur—namely T_s=445°·2, instead of the value 444°·53, as obtained by Callendar and Griffiths, are shown in the following table.

Corrections applicable to Temperature measured by the Platinum Thermometer, assuming

$T_s = 444^{\circ}\cdot53$, the value of δ being 1·500,

to transform them to the new scale, where

$T_s = 445^{\circ}\cdot2$, and δ would become 1·538.

	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.	80°.	90°.
−0	0·000	+0·004	+0·009	+0·015	+0·022	+0·029				
+0	0·000	−0·004	−0·006	−0·008	−0·009	−0·010	−0·009	−0·008	−0·006	−0·003
100	+0·000	+0·004	+0·009	+0·015	+0·022	+0·030	+0·038	+0·047	+0·058	+0·069
200	+0·031	+0·093	+0·107	+0·122	+0·148	+0·164	+0·171	+0·189	+0·209	+0·229
300	+0·250	+0·272	+0·295	+0·319	+0·344	+0·370	+0·397	+0·426	+0·455	+0·486
400	+0·517	+0·549	+0·583	+0·613	+0·653	+0·690	+0·728	+0·768	+0·808	+0·849
500	+0·89	+0·94	+0·98	+1·03	+1·07	+1·12	+1·17	+1·23	+1·28	+1·33
600	+1·39	+1·44	+1·50	+1·56	+1·62	+1·69	+1·75	+1·81	+1·88	+1·95
700	+2·02	+2·09	+2·16	+2·24	+2·31	+2·39	+2·47	+2·55	+2·63	+2·71
800	+2·80	+2·89	+2·97	+3·07	+3·16	+3·25	+3·35	+3·45	+3·55	+3·65
900	+3·75	+3·85	+3·96	+4·07	+4·18	+4·29	+4·41	+4·53	+4·65	+4·77
1000	+4·89									

Sèvres, March 1900.

Discussion.

Prof. Callendar said that he was unable to agree with the correction to his observations suggested by M. P. Chappuis. He considered that the uncertainty in the coefficient of expansion of the gas was due to uncertain changes in the volume of the bulb, and to uncertainty in the coefficient of expansion of mercury. The fundamental coefficient of mercury was ·00018153 according to Regnault, ·00018216 according to the later reduction of Broch, and ·00018256 according to experiments by Chappuis with a hard glass bulb. It made a difference of no less than 4 per cent. in the fundamental coefficient of expansion of the glass, according as the original results of Regnault, or the value found by Chappuis, assuming the linear expansion of glass, were adopted. The importance of the changes in the volume of the bulb had been fully pointed out and a method of taking approximate account of these changes had been explained in the paper on the boiling-point of sulphur in 1890. Unfortunately the glass employed was rather soft, and the changes of volume which occurred were too great to permit of the most accurate determination of the coefficient. Subsequent experiments with a more accurate apparatus in 1893, which had not yet been published owing to the uncertainty of the expansion correction, pending some experiments on the absolute expansion of mercury, showed that the coefficient of expansion of air in a thermometer dried under similar conditions to that used in 1890, was slightly smaller than that which had been assumed (·0036720 instead of ·0036749). The 1893 experiments also gave a lower value for the boiling-point of sulphur, which was directly observed on several occasions, with the air-thermometer in the boiling sulpbur, as well as the platinum thermometers. The difference, however, was less than the uncertainty of the expansion correction. The 1893 results depended on assuming the expansion of mercury, by which the expansion of the bulb was determined; and the results, when extrapolated to 445° C., differed by nearly a whole degree according to the empirical formula chosen to represent the expansion of mercury. It appeared probable that the small error in the coefficient of expansion adopted in 1890 was due to an uncertainty in the volume of the bulb, and that the value 444·53 for the boiling-point of sulphur should be *lowered* by about a quarter of a degree. Since, however, this correction was opposite to the correction for the constant-pressure air-scale, as calculated from the experiments of Joule and Thomson (Phil. Trans. 1887, p. 179), and since the expansion of the bulb used in 1893 was so uncertain, owing to extrapolation, it appeared preferable to await further experiments, rather than publish so small and uncertain a correction. The instrument used in 1893 had since been reconstructed of Jena glass, and the experiments had been repeated with great care by Mr. Eumorfopoulos. The uncertainty in the expansion of mercury still remained; but assuming Broch's reduction of Regnault's experiments, and extrapolating the formula for the expansion of glass obtained over the range 0° to 184°, the value of the boiling-point of sulphur deduced came out even lower than from the 1893 observations with the lead-glass bulb. The difference of the results was due entirely to the smaller correction for the expansion of the bulb.

With regard to porcelain, Prof. Callendar did not consider it to be at all a good material for these experiments, owing to the difficulty of the glaze. Inequalities of thickness of glazing produced uncertainties in the expansion, and the smallest imperfection in the glazing of the interior might produce very serious effects. He did not think that the average coefficient of a tube or bulb over a large range of temperature, could be fairly inferred from the behaviour of a small and possibly asymmetric specimen. It was hardly possible that the rapid rate of change found between 0° and 80° in the recent experiments of M. P. Chappuis, which was six times as large as that found by Bedford for the whole tube over the range 0° to 800°, could be considered to be applicable to the whole tube, and to the whole range of Bedford's experiments. No doubt different specimens of porcelain differed considerably in their coefficients, but the difference over the whole scale was not likely to be so great as that implied by the difference between the determinations of Bedford and Chappuis. Bedford's formula, extrapolated from 800° to 1000°, made the average expansion of this tube from 0° to 1000° but slightly greater than that determined by Deville and other observers. But if it were considered justifiable to extrapolate that of Chappuis over the same range, the resulting expansion would be nearly three times as great as that found by Deville, which appeared to be unlikely. He considered that extrapolation over so large a range from observations confined to the limits 0° to 80° was not in reality justifiable, especially in the case of a heterogeneous material like porcelain, although it might give less inconsistent results in the case of homogeneous and well-annealed metallic bulbs.

The correction for the expansion of the bulb was, he believed, given correctly by the expression

$$dt=(c+b\theta)\,t\,(t-100),$$

as explained in the paper on "The Practical Thermometric Standard" (Phil. Mag. Dec. 1899). He did not agree with M. P. Chappuis that the correction was independent of the value of the fundamental coefficient c, although the value of b was certainly most important at high temperatures, as shown by the formula. He also wished to take exception to the method adopted by M. Chappuis of calculating the correction of the nitrogen thermometer to the absolute scale. According to the experiments of Joule and Thomson, the correction should be greater; according to other authorities it might be less. He had no doubt himself that Joule and Thomson were more nearly correct than Van der Waals, but this was rather a difficult question, and he hoped to be able to discuss it more fully in a future communication.

Mr. Glazebrook said that, although he placed confidence in Chappuis' formula for a definite piece of porcelain between certain temperatures, he thought further and careful work was necessary before fixing on a formula for use over the wide range covered by the experiments under consideration.

Prof. Carhart said he would like to see a comparison made between the results of experiments with gas-thermometers and those with platinum or platinum-rhodium couples.

Mr. Rose-Innes expressed his interest in the behaviour of nitrogen about 100° C., as mentioned in M. Chappuis' paper.

29

XXVII. *On the Controversy concerning Volta's Contact Force.*

By Professor Oliver Lodge, *D.Sc., LL.D., F.R.S.*[*]

Chapter I.

Thermodynamic Arguments.

Those who take what I may call a metallic view of the Volta contact-force are accustomed to deny that the Peltier evolution of heat measures the local E.M.F. existing at a junction ; they assert instead that it measures the rate at which that same E.M.F. varies with temperature :—

$$\Pi = T\frac{dE}{dT}.$$

Let us examine this assertion.

An equation of this general shape is undoubtedly true, but it has not the meaning which they assign to it.

The Π may refer to a particular junction, and in certain cases does, but the E does not. The E means the total E.M.F. of the complete circuit, always.

I venture to think that this will not be disputed, if the matter be for a few moments carefully attended to. To assist attention we may go carefully over some elementary ground—so elementary that it is difficult to secure for it that amount of attention which is necessary for clearness.

The thermoelectric power of a metal A at various temperatures means the function which is plotted in an ordinary thermoelectric diagram, with temperatures as abscissæ, relatively to some standard metal (lead) taken as the line of reference or constant zero of thermoelectric power.

To determine this function a circuit has to be constructed with the metal A and the standard metal O, their junctions brought to different and known temperatures t and t', and the resulting E.M.F. (the whole E.M.F. of the circuit) observed, being measured either by the strength of current developed, or better, by a potentiometer or compensation method. Then the ratio $E/(t'-t)$ is called the thermoelectric power of the metal A at the mean temperature $\frac{1}{2}(t+t')$, and is plotted accordingly, for a considerable range; the differences $t'-t$ being naturally kept small, in case the resulting function is not linear.

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[*] The Presidential Address delivered at the Annual General Meeting, February 9, 1900.

This is done likewise for other metals, B, &c.; and the relative thermoelectric power of two metals at the same temperature (being $P_{AB}=P_B-P_A$) is represented by the vertical distance between the A and B lines of the diagram.

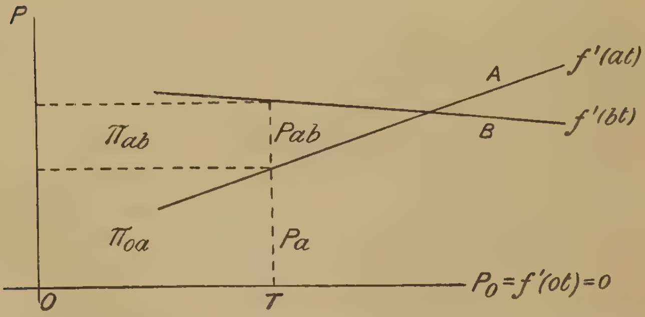
Another function of temperature is likewise represented in the diagram, not by a length but by a rectangular area, bounded on the right by the thermoelectric height, and on the left by the line of absolute zero. This is the function Π, such that

$$\Pi_{OA}=P_AT, \quad \text{and} \quad \Pi_{AB}=P_{AB}T.$$

It is to be observed that in this diagram (apart from the experimental mode of obtaining real values for P) no reference is so far made to any junctions, nor to any circuit, nor current, nor E.M.F., nor evolution of heat; it represents nothing but a geometrical plotting of certain metallic properties as functions of absolute temperature.

If we now connect the two metals at one point, they are necessarily at the same temperature, say T_1, at that point; their relative thermoelectric power at the junction, P_{ABT}, may be called P_1; and the area just spoken of is $\Pi_1=P_1T_1$.

Fig. 1.



Now Lord Kelvin showed in 1856 that this Π_1 is the Peltier coefficient, *i.e.* that it measures the reversible heat generated at the junction if a unit quantity of electricity is transmitted across it.

If we proceed to connect the two metals also at some other point, at some other temperature T_2, there will of course be an appropriate value for P_2 and Π_2, but there is more than that: every intermediate point of one metal will have a temperature corresponding to that at some intermediate point of the other metal, and accordingly there is a P and a Π appropriate to every intermediate temperature.

There will also be now a closed circuit, and a current, driven by a resultant electromotive force, which may be expressed instructively in the following different ways,

$$E_{AB} = \text{cycle}\int P\,dt = \int_1^2 P_{AB}\,dt = \int_1^2 \Pi\, d\log T = f(t_2) - f(t_1)\;;$$

the function f being such that

$$\Pi_{AB} = Tf'(t) = T\frac{d}{dt}E_{AB} \text{ everywhere.}$$

At the junctions there is now a reversible generation of heat per second

$$\Pi_1 = T_1 f'(t_1) \quad \text{and} \quad \Pi_2 = T_2 f'(t_2)$$

per unit current.

In the metals there is likewise a reversible generation of heat

$$\Theta_a = \int_1^2 \sigma_a\,dt, \qquad \Theta_b = \int_1^2 \sigma_b\,dt,$$

such that

$$\sigma_a - \sigma_b = T\frac{d^2E}{dT^2} = Tf''(t)\;;$$

and the total E.M.F., in addition to the modes of writing adopted above, may also be represented as,

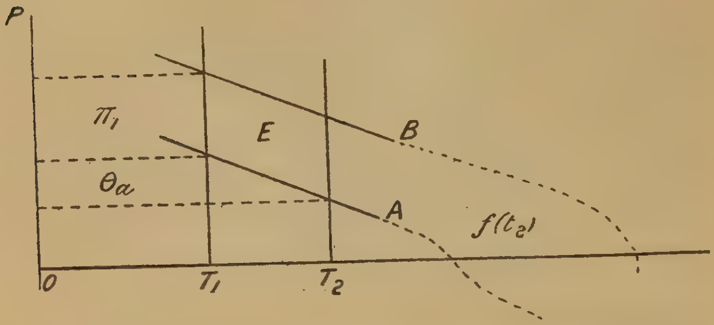
$$E = J(\Pi_1 - \Pi_2 + \Theta_a - \Theta_b),$$

since E represents the work done per unit quantity of electricity conveyed.

The representation of all this in a thermoelectric diagram is neat and convenient, and is sufficiently shown in the figure, without overlapping of areas.

Remembering that it is P which is plotted vertically, and that $P = \Pi/T$ everywhere, the whole of the above various expressions for the area E are geometrically represented.

Fig. 2.



The only one needing explanation is the expression $f(t_1) - f(t_2)$, the difference of two indefinite-integral areas, of which the second limit is incomplete in the figure, because unknown. All that is known about $f(t)$ is that E is the difference between its values at the temperatures t_1 and t_2, that $f'(t) = \Pi_{AB}/T$ everywhere, and that $f''(t) = (\sigma_a - \sigma_b)/T$ everywhere. But the value of the function $f(t)$ itself is not known; nor is there any means of determining it from observed values of a current in a closed thermoelectric circuit. (I have no reason for depicting this area in the diagram on the right towards infinity, instead of on the left towards absolute zero, except that thereby overlap is avoided. Otherwise one would naturally draw it so as to be bounded hypothetically by the line of absolute zero. The diagram does not attempt to represent its probable value, but merely to emphasize the fact that its absolute value is not known or needed in ordinary thermoelectricity.)

Excepting in portions relating to $f(t)$ there is, I apprehend, so far no controversy. And yet, if all this be admitted, my contention that, in the equation $\Pi = T dE/dt$, the E refers to the whole circuit and not to any particular part of it, though the Π *may* refer to a junction, is substantiated.

Nevertheless this statement has been, and probably still will be, seriously disputed *, but I hope that if it is still disputed the actual subject will be dealt with, and not hydraulic illustrations of doubtful applicability given.

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* For instance, I might quote several physicists who have said (somewhat casually, as I think), since a discussion at the Institute of Electrica Engineers (Journ. Inst. E. E. 1885), that the Peltier heat-evolution is no measure of a contact E.M.F. existing at the junction where it occurs, but is a measure of the rate of variation of this E.M.F. with temperature; but it will suffice if I quote part of Prof. Ayrton's remark in that same discussion, with an occasional interposition of my own in square brackets, because he expresses himself clearly and strongly—always a desirable thing to do:—

"Dr. Lodge's fundamental argument—the argument in fact upon which his whole paper is based—is this: He *assumes* that in all cases where there is a considerable difference of potential at a [metallic] junction, heat or cold must be developed when a current flows across that junction." [I should myself word it rather differently, to avoid misunderstanding, though misunderstanding is hardly possible in what follows; but apart from possible misunderstanding I have no objection to the statement, except that I do not regard it as an *assumption*, unless the conservation of energy is an assumption.] "He states what is quite true and well known—that practically no heat is developed when a current flows from zinc to copper across the junction; therefore he concludes that there can be no contact-potential difference at this junction like three-quarters of a volt. But this reasoning is based on a totally wrong conception of the Peltier effect, which I am astonished to find exists in the mind of a man with the scientific powers of Dr. Lodge. *The amount of heat generated when a unit current is sent through a junction for a second is undoubtedly the measure of the coefficient of the Peltier effect; but this coefficient is in no sense a measure of the contact-potential difference existing at the junction.*" [Italics are Prof. Ayrton's.] "What the Peltier effect, at a junction of the two substances at a given temperature, measures, is the product of the absolute temperature into the rate of variation, with temperature, of the contact-potential difference at that temperature; in other words, if Π is the Peltier effect at a junction which is at an absolute temperature t, and if V is the contact-potential difference at that temperature, $\Pi = t\frac{dV}{dt}$.

"Hence the magnitude of Π does not measure V, but merely $t\frac{dV}{dt}$, and the error of Dr. Lodge is of the same sort of order as saying that a train going at a very nearly uniform speed is necessarily moving very slowly because the change of speed per second is very small. This disposes of the objection based on the smallness of the Peltier effect." [No, it is not disposed of quite so easily as that. The difference between velocity and acceleration is somewhat familiar.]

Controversy begins as soon as localization is attempted; as soon as one says that $J\Pi_1$ is a measure of the E.M.F. existing at the junction whose temperature is T_1, and that $J\Theta_a$ is a measure of the E.M.F. existing along the gradient of temperature in the metal A.

Controversy also begins in respect of the function $f(t)$ [*]. There are those who decline to take an agnostic position with respect to the absolute value, or second limit, of this function, and who say that it represents absolutely the Volta contact force; that is, the E.M.F. observed in the dielectric space between two metals when a metallic circuit is not completed, when there is only one metallic junction, and when a dielectric space is substituted for the other junction. The value of the E.M.F. thus observed is very large, say a thousand times as big as any we have been so far dealing with; it is not observable in any closed metallic circuit, it is only observable in a dielectric portion of a circuit; and it has no apparent connexion with thermoelectricity; hence, those who assert that this great E.M.F. is represented by $f(t)$, that is, by a function of the metallic junctions otherwise and solely known by its differences and derivatives in thermoelectricity, should be prepared with a definite proof of their statement. So far as I know a proof has never even been attempted. To me it appears that the introduction of a dielectric or an electrolyte into the circuit, with its necessary two new junctions, each with chemical potentiality, has entirely altered the whole conditions; and that no longer can it be said that the above laws, appropriate to a closed metallic circuit, apply. I maintain that whether the assumption, that $f(t)$, a function of the metallic junctions alone, represents the Volta effect observed in the air when a circuit is broken, is made tacitly or explicitly, it is made gratuitously and requires justification, which, so far as I know, has not yet been forthcoming.

To show that the unsupported statement just referred to —whereby the Volta effect, a potential gradient observed in the air when a metallic circuit is broken, is introduced into a thermoelectric function of metals alone, with which it appears to me to have nothing to do—is responsibly made, I might quote from several writers; but there is no need to quote more than Lord Kelvin's statements in his Friday evening discourse to the Royal Institution for May 1897 (Reprinted in the Phil. Mag. July 1898) :—

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[*] *Cf.* Phil. Mag. March 1886, p. 267.

"§ 19. Seebeck's great discovery of thermoelectricity (1821) was a very important illustration and extension of the twenty years' earlier discovery of the contact-electricity of dry metals by Volta. It proved independently of all disturbing conditions that the difference of potentials between two metals in contact varies with the temperature of the junction." [This is no doubt true as it stands, if the junction is the only part heated; the Seebeck force is superposed upon the Volta force, and hence the electrostatic effect observable in an incomplete circuit is naturally slightly affected by differences of temperature, though not necessarily by absolute uniform temperature. The break of circuit may be made in the middle of one of the metals whose junctions are maintained at different temperatures, in which case only the Seebeck force could possibly be electrostatically observed (that is, a combination of Peltier and Thomson effects) by a sufficiently sensitive electrometer; or the break may be made between the two metals, in which case the much greater Volta force will be observed in the air-gap in combination with the insignificant Peltier force of the metallic junction; and any fluctuation of temperature to which that remaining metallic junction is subjected will but vary this insignificant superposition upon the true Volta effect. But the sentence quoted is not intended to convey this meaning; what it is intended to convey is that the Volta gradient of potential observed in the gap is chiefly due to something occurring at the remaining metallic junction, and that this something is a function of the temperature. Indeed, a later sentence (§ 26) clearly states, not only the existence of this large metallic-junction force, but also its cause.] "This force" [viz. the force of attraction between the oppositely-charged metals across a gap], "properly viewed, is a resultant of chemical affinity between thin surface-layers of the two metals."

[And then the author goes on to explain that the junction-force at the boundary of two metals has nothing whatever to do with any reversible heat-effects which may be observed there; because, if it had, these reversible heat-effects would be vastly larger than in fact they are. It is therefore argued that these Peltier effects by no means represent the value of the E.M.F. existing at the junction where they occur, but represent only the rate at which this E.M F. varies with temperature, $\Pi = TdE/dT$; whereas, as I have said above, the E really appropriate to this equation is not located at the junction at all, but is the resultant or integrated E.M.F. of the whole circuit. However, I continue the quotations, not at first using quotation marks simply because the wording is abbreviated where no precision is required.]

Imagine a circuit of two metals—say iron and copper; and let the copper be cut across in the middle, so that an independent E.M.F. can be introduced by wire electrodes and a current maintained across the two junctions. "The Peltier heat produced where the current passes from iron to copper is manifestly not the thermal equivalent of the work done." [This sentence is ambiguous. It may mean the "work done" on the *whole circuit*, in which case it is true; it may mean the "work done" precisely *at the junction*, in which case I should say that the word "not" ought to be omitted. The immediate context suggests the former interpretation; the next succeeding context suggests the latter. The immediate context runs as follows:]

"In fact, if the two junctions be at equal temperatures, the amounts of Peltier heat produced and absorbed at the two junctions will be equal, and the work done by the independent E.M.F. will be spent solely in the frictional generation of heat." [This is undeniable, though not apparently to the point; but the next section continues]

"Many recent writers, overlooking . . . obvious principles, have assumed that the Peltier evolution of heat is the thermal equivalent of E.M.F. at the junction. And in consequence much confusion, in respect to Volta's contact-electricity and its relation to thermoelectric currents, has clouded the views of teachers and students. We find over and over again the statement that thermoelectric E.M.F. is very much smaller than the Volta contact E.M.F. of dry metals. The truth is, Volta E.M.F. is found between metals all of one temperature, and is reckoned in volts, or fractions of a volt, without reference to temperature." [Certainly.] "If it varies with temperature, its *variations* may be stated in fractions of a volt per degree." [By all means.] "On the other hand, thermoelectric E.M.F. depends essentially on *difference* of temperature" [the thermoelectric force of a complete metallic circuit does, and not the thermoelectric force at any particular junction; that depends on the temperature of the junction, and cannot be affected by the temperature somewhere else] "and is essentially to be reckoned *per degree*; as, for example, in fraction of a volt per degree." [Not so; an electromotive force of any kind whatever must be reckoned in volts. Volts per degree is not E.M.F., but is the so-called relative thermoelectric power of two metals.]

I have ventured thus to interpolate what I consider corrective remarks in brackets into this readily accessible quotation, because of a preceding sentence with which I quite agree, viz. this:—"Peltier's admirable discovery . . . is highly important in theory, or attempts at theory, of the contact electricity of metals"*.

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* To this I might add, what I now see more clearly than before, that it is more particularly the mode of statement of Lord Kelvin's own "admirable discovery" that is really the central feature of this part of the controversy. For there are three, at least three, modes of regarding it:—

1st. A convection of heat pure and simple—electricity acting as a fluid with a positive or negative specific heat, and conveying heat down or up a temperature gradient.

2nd. An E.M.F. acting in metal from hot to cold or from cold to hot, and thereby either opposing or assisting the passage of a current, in the one case developing extra local heat, in the other case consuming heat or developing local cold, proportional to the local E.M.F. and the current.

And this 2nd mode has two subdivisions:—The E.M.F. thus supposed to exist from end to end of a metal bar with its ends at different temperatures, may display itself:—

either (*a*) as a gradient of potential in the air outside, detectable by an abnormally sensitive electrometer-needle, but never yet observed;

or (*b*) as a change in the step of potential from metal to air, according to the temperature of the metal; the air-potential outside being left uniform.

But there is yet the third method of regarding the whole matter:—

And in case anything that I can say can make the matter clearer, I would reassert that since E.M.F. is work per unit charge conveyed, not only for the whole circuit but for any

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3rd. As a mere modification of the junction E.M.F. with temperature; so that the Peltier function, which had been of the value $kt(t_0-t)$, is modified by addition of a term $\frac{1}{2}kt^2$, so that it becomes $kt(t_0-\frac{1}{2}t)$.

On this plan, no E.M.F. of any kind is supposed to exist in the single metal itself, no more than when its temperature was uniform; all the E.M.F. is thrown upon the junctions; the E.M.F. of the circuit is simply the difference of the junction-forces, as it would have been had there been no Thomson effect; but each junction-force, by reason of the Thomson effect, has somehow attained a quadratic term; their difference therefore permits thermoelectric reversals and the observed law of the thermoelectric circuit, for subtracting the two junction-forces we get

$$E=k(t_1-t_2)(t_0-\bar{t}).$$

This third mode is evidently the way in which several philosophers have been accustomed to regard the matter; and on the hypothesis that junction-forces in a metallic circuit are due to the affinity of metals for each other, it is natural to locate all the E.M.F. at the junction of two different metals, and to deny any E.M.F. between different parts of one and the same metal at different temperatures. (This is very different from the experimental fact that the resultant E.M.F. round a homogeneous metallic circuit is zero.) Those who regard the junction-forces as physical would naturally take a different view. For instance, take Helmholtz's hypothesis of a specific attraction of metals for electricity, the same being a function of temperature: a differential attraction between the hot and cold ends of a bar would be just as essential as a differential attraction at the junction of metals of different kinds. It has been asserted that Helmholtz's view tends to concentrate the force at the junctions and to make the Peltier heat proportional to the rate of variation of the local junction-force with temperature. But even if it does, and later we will show that it does not, no view makes this junction-force the same as the Volta effect, or suggests that the Volta effect has anything to do with the matter; except on the hypothesis that the air layer intervening when a metallic junction is broken is utterly inert and impotent.

It is no argument in favour of the impotence of the air layer to say that it produces no apparent effect when it bathes the metal uniformly all round; the question is what it does when uniformity all round does not exist. Balanced forces are not the same thing as no force, although they produce the same zero accelerative effect. Nor does the absence of acceleration prove the absence of all force. A body subject to balanced forces and obeying the first law of motion is a frequent spectacle—a railway train or a snowflake for instance—but a body subject to no forces is decidedly rare.

portion of a circuit, and since a unit charge conveyed across a junction develops an amount of heat $\pm\Pi$, it follows that the physical E.M.F. located at that junction is measured by and is equal to $\mp J\Pi$ (assisting the current in one direction and thereby consuming heat or developing cold, opposing it in the other direction and therefore developing extra heat); unless some other mode of accounting for the appearance or non-appearance of the reversible heat is devised, or unless the reversible energy takes some other form than heat.

Wherever energy appears or disappears in a circuit, there, in that place, must be located an E.M.F. It may be, so to speak, the frictional E.M.F. appropriate to Ohm's law in a homogeneous conductor; it may be the chemical E.M.F. at a fluid or semifluid junction discovered by Volta; or it may be the contact-force at a solid junction, of which the integral round a whole circuit of non-uniform temperature was discovered by Seebeck, the locality of part of that E.M.F. by Peltier, and the locality and existence of the rest of that E.M.F. by Lord Kelvin.

At a chemical junction the reversible energy need not all of it or much of it take the form of heat, and in that case the major part of the E.M.F. may be rightly called chemical, not physical; but at a metallic junction, as in a homogeneous conductor, heat is usually the only form of energy expected or observed, and in that case wherever the E.M.F. is located there the heat or cold must appear. The ordinary way out of this conclusion is to suppose that electricity is a fluid with a real specific heat whose value changes from metal to metal, so that heat can be evolved or absorbed at a junction by a sudden change in the heat-capacity of the electric fluid flowing across it, without the need for any local performance of work or any corresponding local E.M.F.*

I should be glad to know whether any objectors to what I may call the Maxwellian view—the view of the precise local correspondence between E.M.F. and reversible heat-effects—do seriously base their opposition on this ground of a real physical specific heat of electricity. The only other alternative that I can see (short of Helmholtz's theory, to be mentioned later) is to say that the metallic junction is really a chemical junction too, that the energy does not take the form of heat because it takes that of chemical combination, and to point to a weighable quantity of alloy or other compound produced at that place by the passage of a current. Whether or not any chemical compounds are really formed at a given junction, then becomes a simple question of fact.

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* *Cf.* Phil. Mag. March 1886, pp. 271–276.

Since a voltaic circuit never has less than three junctions, and since we are trying to apply to it as much of the thermoelectric laws as it will stand, it may be well to write down these laws for the case of a metallic circuit with any number of metals, and therefore with a thermoelectric diagram having discontinuities at the several junctions,—everything discontinuous but temperature. Each metal, referred to the standard, has a certain thermoelectric power at each temperature, and accordingly the resultant E.M.F. of the circuit is

$$\mathrm{E} = \text{cycle}\int \mathrm{P}\,dt.$$

We may also express the E as a sum of the E.M.F.'s at the several localities, the junctions on the one hand, and the temperature-gradients in the metals on the other; so that

$$\mathrm{E} = \Sigma(\Pi) + \Sigma(\Theta).$$

Further, as regards the Π function of each metal relatively to the standard

$$\Pi_{oa} = \mathrm{P}_a\mathrm{T} \text{ everywhere};$$

and also

$$\Theta_a = \int_1^2 \sigma_a dt\,;$$

so, maintaining this reference to the standard, it is still true that

$$\mathrm{E} = \Sigma\int \Pi\, d\log\mathrm{T}.$$

But Π_{ab}, though still equal to $\mathrm{P}_{ab}\mathrm{T}$, is no longer equal to $\mathrm{T}d\mathrm{E}/d\mathrm{T}$, unless by E is meant E_{ab}, that is the E.M.F. of a non-existent small portion of circuit formed solely of the two metals A and B.

The fact is, that at a junction there are now three values of P and of Π, viz. Π_{oa}, Π_{ob}, Π_{ab}; and it is only when we constantly maintain the reference to the standard metal *o* that we can say $\mathrm{E} = \Sigma\int\Pi\,d\log\mathrm{T}$; otherwise there are discontinuities not allowed for. We cannot say that

$$\int_1^2 \frac{\Pi_{za}}{\mathrm{T}}dt + \int_2^3 \frac{\Pi_{ab}}{\mathrm{T}}dt + \int_3^4 \frac{\Pi_{bc}}{\mathrm{T}}dt + \ldots\ldots + \int_n^1 \frac{\Pi_{yz}}{\mathrm{T}}dt$$

is equal to E. For one thing, the temperature-limits and the junctions do not fit. An expression of the form $\int_{t_1}^{t_m}\frac{\Pi}{\mathrm{T}}dt$ can still be employed for E when care is taken to arrange the Π/T so as to represent the difference in thermoelectric powers between pairs of points of the circuit which are *at the same temperature*, whether the metals possessing that temperature happen to be anywhere directly in contact or not. With this precaution, the integration can proceed over a discontinuity at every junction; but, in order to select the appropriate temperature-limits, either reference must be made to the real temperature of different parts of the circuit, or else the simple plan of referring everything to a hypothetical standard metal lying along the axis of temperature must be employed.

This being understood, we can still write $\Pi/T=dE/dT$; but, while the E refers to the whole circuit, the Π does not now refer, even permissibly, to the junctions; except the hottest and coldest junctions; unless reference is made continually to the standard metal (some point of which is necessarily at the same temperature as any given junction), and not to the particular pair of metals which happen there to touch.

Hence we may not assert of the actual junctions at different temperatures that $\Sigma(\Pi)=\Sigma(TdE/dt)$; nor can we assert without caution that $\Pi=TdE/dt$ at each junction individually.

So far for a multiple metallic circuit.

If the circuit is not wholly metallic, but is partly dielectric or electrolytic, the introduction of the extraneous substance complicates matters. There may be a resultant E.M.F. now without any difference of temperature; and this E.M.F. may be partly chemical and partly physical, partly $\Sigma(J\theta\epsilon)$, to use the customary notation (Kelvin, 1851), and partly $\Sigma(J\Pi)$. For even if the temperature is everywhere uniform, it is no longer necessary for the Π's to balance each other; all one can be sure of is that when there is no gradient of temperature there can be no Thomson force Θ; and that the resultant E.M.F. is therefore the algebraic sum of the junction forces,

$$E = \Sigma(J\Pi) + \Sigma(J\theta\epsilon).$$

It cannot now be assumed without further special proof that at any given junction $\Pi=TdE/dT$; nor can we assume that it is permissible to individualise the junctions; but still, for an electrolytically closed circuit at uniform temperature, von Helmholtz has shown that taking *all* the junctions into account,

$$\Sigma(\Pi)=T\frac{dE}{dT},$$

the E being the resultant E.M.F., the sum of the contact-forces at *all* the junctions whether they be of a chemical or physical nature. And recently (Proc. Roy. Soc. Edin. Feb. 7, 1898, vol. xxii. p. 118, "On the Thermodynamics of Volta

Contact Electricity") Lord Kelvin has proved exactly the same thing to hold for a dielectrically closed circuit of uniform temperature likewise. The argument in this case he considers quite rigorous, because there is now no questionable gradient of temperature along heat-conductors, and therefore no necessarily concomitant irreversible effect; and therefore no question of whether such effect be accidental or essential.

The only loophole I can perceive for a flaw in the reasoning is the possibility that the heat of chemical combination varies for small temperature changes, *i. e.* that it is a perceptible function of the temperature; and I have no reason for pressing this, or for hesitating over accepting the above conclusion to the utmost, so long as the temperature is uniform.

It is unimportant for the present argument, but it may be worth while to notice in passing, that no such relation as $\Sigma(\Pi)=\Sigma(\mathrm{T}d\mathrm{E}/dt)$ has ever been proved for a complex circuit in which differences of temperature are superposed upon other sources of electromotive force. And from what has been said in similar small type just above, no such relation can truly be asserted, without considerable care as to the form of the statement. Its most obvious signification, having reference to the actual junctions, would not be correct. It is to be observed that in the Kelvin and Helmholtz expression for a complex circuit at uniform temperature, the meaning of $d\mathrm{E}/dt$ is a change of E.M.F. of the circuit per degree caused by the passage of a current—caused, that is to say, by a thermal polarization: the dt/T being the efficiency of a cyclical Carnot engine. Whereas in such an expression in ordinary thermoelectricity as $d\mathrm{E}/dt=\mathrm{P}=\Pi/\mathrm{T}$, the meaning of $d\mathrm{E}$ is the total E.M.F. observed in a circuit of two metals when its pair of junctions are artificially maintained at a difference of temperature dt.

It may be said that these two meanings are after all the same: and so they are in a simple circuit of two metals, but not in a complex circuit with junctions at more than two temperatures.

But what has all this to do with the localisation of E.M.F. at a given junction? Admitting, and indeed teaching, all this, I still hold that the reversible heat at a specified junction is a measure of the metallic E.M.F. located there. That in fact at a metallic junction $e=\Pi$, or $\mathrm{J}\Pi$ if anyone thinks it worth while in a matter of this sort to trouble about practical laboratory units.

Those to whom I referred in the opening paragraph of this communication make the mistake of confusing e with E,—confusing the E.M.F. at any one junction with the whole E.M.F. in a circuit. If they do this, they naturally beg the question, and of course locate the whole E.M.F. at the particular junction which takes their fancy at the moment: usually an interface of zinc and copper.

The truth is that $E = \Sigma(e)$ always; but only in a metallic circuit at constant temperature does $\Sigma(e) = \Sigma(\Pi)$; just as only at a metallic junction does $e = \Pi$ individually. At an electrolytic or dielectric or what I may call a chemical junction, that is one with chemical potentialities, the E.M.F. is not purely thermal, and hence is not measured by the Peltier effect; it is chiefly of chemical origin and is calculable from the energy of combination of the materials on either side the boundary.

Observe I do not say that at such a junction there need be any chemical *action* (at least not any completed chemical combination in the ordinary sense) to account for the E.M.F., but there is the possibility of chemical combination; and there will be actual chemical combination if a finite quantity of electricity is transmitted across it. For conduction in an electrolyte is convective in its nature; whatever electricity travels, the material atoms travel with it; and the travelling of oppositely charged ions in opposite directions involves chemical action at a liquid junction, involves transfusion of substance, involves what is practically, and may be actually, chemical recombination. Possibly something of the same sort may be said, less positively, about electric displacement at a dielectric boundary.

But at a metallic junction there is no such chemical potentiality. You may pass a strong current across a zinc-copper junction for years and you will not get any brass. I would not deny that there may be a kind of material or "corpuscular" interchange even here: in fact in the light of recent most interesting work by J. J. Thomson it is probable; but the corpuscles thrown across the junction from zinc become copper; and *vice versa*, those dissociated from a copper atom settle into their new places as part of a zinc atom; there may thus be a tendency to an ineffective kind of *transmutation*, but there is no tendency to alloy. (See below, p. 420.)

Why then if a metallic junction is chemically inert should it ever be held that the chemical affinity of zinc for copper is the propelling influence which causes the E.M.F. located at such a junction? What has ordinary chemistry got to do with this metallic E.M.F.? I echo the question, and proceed to my second chapter.

Chapter II.

The facts of Contact Electricity.

Some people (for whom I have a great respect), on the strength of the fact that metals in contact attract each other, maintain that this accounts for their tendency to combine and for their heats of combination, as well as for the value of their contact E.M.F.

Now, that metals in contact attract each other I fully admit. They must, because they are oppositely charged. There was a time when people disputed the *fact* of the Volta effect, but I am not one of those, and never was. All the facts by which Lord Kelvin or anyone else properly displays the Volta effect I fully admit, and am accustomed to show to my class; though indeed in Lord Kelvin's Friday evening Royal Institution discourse (Phil. Mag. July 1898) they are described anew with admirable clearness and precision. To avoid any possible mistake on this score, I will briefly recapitulate the facts.

Dry zinc and copper in dry air brought into contact become oppositely charged. If their surfaces are arranged so as to form a condenser of reasonable capacity, the charges may be large. When they are separated adroitly, the charges remain on the metals and raise them to a high (numerical) potential which may readily be displayed by an electrometer or even a gold-leaf electroscope.

A trace of moisture, *i. e.* of liquid electrolytic moisture, not dry vapour, may be fatal to the success of this experiment; for if a drop of liquid intervenes and connects the two metals momentarily, after the true metallic contact has been broken, nearly all their charge leaks across this conducting-bridge; and the resulting charge, and therefore the resulting potential of the separated plates, is extremely small. A water junction between two plates has no appreciable power of charging them oppositely; practically no more power than air has. In many respects a water intervention acts very like an air intervention; in one respect only does it strikingly differ:—its conductivity enables it to abolish any effective display of the opposite charges otherwise produced, *e.g.* by metallic contact. The same detrimental influence is exerted by the conductivity induced in air subjected to the action of x- or of uranium rays; such air behaves precisely like a badly conducting electrolyte. Nothing further need be said to make clear the action of metallic uranium for present purposes.

It is remarkable, in practice, how imperceptibly minute the quantity of liquid may be, in order thus to act detrimentally. But after all it is only a question of arithmetic:—

Let z be the average thickness of dielectric intervening between the zinc-copper plates, during their so-called close contact, everywhere except at the place where they really effectively, *i.e.* metallically, last touch as they are being separated; and let z' be the distance between the same surfaces at the instant when the hypothetical moist or liquid connexion is likewise last broken; then in the dry case the resultant charge is inversely proportional to z, being in fact of the order $\frac{r^2}{1200z}$ electrostatic units, for the usual case of circular disks; whereas in the moist case z' must be substituted for z.

Now a very minute drop of liquid pulls out before it snaps into a column π tenths of a millimetre long, which then represents z'; whereas the dry z may be a tenth or even a hundredth of this magnitude, with well-made plates and careful manipulation.

I have emphasised this to negative any possible idea that I regard moisture as an adverse fetish, acting discontinuously. It is better away; but, if it exists, its detrimental effect is a mere arithmetical affair.

No one, I hope, can now suppose that I imagine that moisture is essential to the success of the experiment, though in his Friday evening discourse to the Royal Institution, May 1897, reprinted in the Phil. Mag. (July 1898), Lord

Kelvin says that there are signs in my British Association Report (Phil. Mag. 1885) of a tendency to fall back upon De la Rive's old [and utterly discredited] hypothesis that the Volta effect was due to oxidation of the zinc by moisture from the air. He means, I expect, that I attach too much importance to the action of oxygen (which may be true: a word on that later), but never have I imagined it to be needed in the form of moisture, nor have I ever wanted the zinc to be actually oxidised. If it be perceptibly oxidised, the Volta effect is diminished.

I say once more—in accordance, I believe, with everybody:—

(1) Two metals connected wholly or partly by liquid are in approximately the same electrical condition as if connected wholly or partly by air. They do not become oppositely charged unless they are at one (or more) point metallically connected: then they do: and in order to be able fully to display this charge on separation, the persistently-connecting medium must be insulating, that is must be dry, *i.e.* free from liquid. It must also be free from high-frequency ætherial radiation or other ionising influence.

(2) If the metals are connected *both* metallically and electrolytically, metallically at one place and electrolytically at another, we have a common voltaic cell and a continuous current.

(3) To complete the statement:—If the metals are connected both metallically and *dielectrically*, that is if they are insulated from each other except at one point where the intervening dielectric is swept away, we have the normal conditions appropriate for a display of the Volta effect: that is, a gradient of potential in the dielectric between them.

The safest and clearest mode of expression is what I have used: the Volta effect consists in an opposite charge acquired by dry zinc and copper while in metallic contact, a charge which results from an E.M.F. of value depending on the condition of their outer surfaces, and controlled solely by this E.M.F. and the electrostatic capacity.

I here avoid any statement involving the term metallic potential, because it is open to misconception owing to variety of definition. Some people prefer to say that zinc and copper in contact are at different potentials, whereas I prefer to say that they are at the same potential so long as they are in contact: but no one can deny that they are oppositely charged.

Some people, again, prefer to say that they are oppositely charged by reason of an E.M.F. at the junction, which keeps them at different potentials: I prefer to say that their charges are distributed so as to enable them to remain at the same potential, in spite of a difference in the specific Volta force existing at the dielectric boundary of each; in other words, that the E.M.F. is at their surface; but again, no one can deny that there exists in the dielectric between them a gradient of potential, the natural result of their opposite charges; which same gradient can cause a charged electrometer needle to move, even without the magnification of potential caused by separation. In fact the magnification of potential by separation does not (within limits) increase the *gradient*, for the potential rises as the capacity diminishes, and so remains in direct proportion to their distance apart, so long as that distance is moderate.

Nor can anyone deny that oppositely charged bodies, or surfaces between which there is a gradient of potential, attract each other. Hence, indirectly, a piece of zinc attracts a piece of copper with which it is at any point in contact; and the attraction increases as the square of the potential gradient, and therefore as the square of the nearness together of the opposed or condenser surfaces.

Signor Majorana (Phil. Mag. Sept. 1899) has designed some simple methods for displaying this attraction, one of them the same as a method I had used for displaying the attraction of two metals exposed to Hertz radiation just before cohesion; viz., a fine metallic fibre hanging in front of a polished facet on a knob, the fibre and its image being watched through a microscope (Discourse on Coherers, Journ. Roy. Inst. 1899): but what has all this to do with the location of contact force at one junction rather than at another? What bearing has it upon the present controversy? So far as I see, none.

And further, I would ask, what has this dielectric attraction got to do with the heat of formation of brass? But in asking this last question I do not pretend that it is an easy one, and I would not dogmatise as to the answer. The question is briefly treated at the end of the present chapter. I only wish to indicate at this stage that the answer to the question is open to doubt, and that it must not be taken as indisputable that the heat of combination of metals has any connexion with their voltaic force, or with their thermoelectric force either.

There was a time when I fancied that though the heat of formation of brass had no connexion with the Volta force, yet it might have some connexion with the thermoelectric force of contact, or, let us say, the Peltier effect. This idea, too, I wish to abandon*, and for the same reason, viz., that if metallic affinity were an efficient agent in propelling the current, then I should expect the transmission of the current to result in some formation of alloy. Conceivably some secondary influence may mask the display of this result; and if the numerical determinations of metallic heats of combination correspond, when reduced to volts, with the E.M.F. anyhow observed in connexion with circuits or partial circuits formed of those metals, that would be a striking coincidence and one to be carefully considered. So far as I am aware, no such coincidence has yet been *indisputably* discovered, even with a single pair of metals.

Experiments on heats of metallic combination have been made by Sir W. Roberts-Austen, by Dr. Galt, by Mr. T. J. Baker, and by Mr. J. B. Tayler. Doubtless also by other workers whom I forget at the moment or do not know of. The results obtained are not yet free from doubt and difference of opinion. Some of the results agree neither with the Volta nor the thermoelectric forces; and this discordance is what I expect will ultimately be believed. On the other hand, some determinations of the heat of alloying of zinc and copper, taken in conjunction with the customary estimate of the size of atoms, do appear approximately to coincide with the order of magnitude of the Volta contact-force. (See end of this chapter.)

If this is truly so, it is very remarkable, and must greatly strengthen the ground of those commonly called "contact theorists." It would seem unlikely to be the result solely of accident. On the other hand, it is undeniable that (either accidentally or otherwise) the order of magnitude of the Volta force can be calculated from the differential heats of combination of the metals for oxygen; which may be written (Zn, O) − (Cu, O). Hence, if it turns out that it can likewise be calculated from the heat of formation of brass (Zn, Cu), it will be either an odd coincidence or it will have an important chemical meaning with regard to heats of combination or chemical affinities in general.

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* *Cf.* Phil. Mag. 1885, p. 356, and Journ. Inst. E. E. xiv. 1885, p. 219.

One way of putting its meaning may be that it tends to strengthen what I may call von Helmholtz's hypothesis *, which can be stated roughly thus :—That the metals do not really attract oxygen, nor do they really attract each other, but that what they attract is electricity; that all chemical attraction, apparently of matter for matter, is the consequence of this real attraction of matter for electricity, the atoms being electrically charged. Further, that the Volta effect is caused, simply enough, by the differential attraction of zinc and copper for electricity. The orthodox way of putting it is as follows :—The zinc attracts positive electricity most; hence, when they are put into contact, electricity flows across the junction and the zinc becomes positive and the copper negative. Another way of putting it is to say that the zinc free surface attracts negative electricity most, and accordingly pulls it in from the space around as soon as the *uniformity* of the force is anywhere interfered with by an inert metallic contact. In either case its ready oxidisability by negative ions is thus explained, and has not to be taken as an independent fact or basis. Whereas, then, I had proposed to calculate the Volta effect as (Zn, O) − (Cu, O), on this view it would have to be reckoned as (Zn, E) − (Cu, E); though what is to be considered precisely as meant by E may be matter for further consideration. I am not going to say anything against this far-reaching hypothesis in a hurry. It demands separate treatment in the light of 'electron' theory.

This is what I intended when I admitted it possible that, as Lord Kelvin said, I had too great a veneration for the need for oxygen in this connexion. The sole reason why I think that it is probably the oxygen film and not the æther discontinuity which causes the force, is that its magnitude corresponds so closely, not only in order of magnitude but in relative details, with the appropriate energy of oxidation. At the same time, if the electrical attraction is the *cause* of oxidation tendency, this quantitative relation is not likely to afford any means of discrimination.

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* Summarised in Phil. Mag. October 1885, p. 378.

The evidence that leads Lord Kelvin to the conclusion that the æther or space or vacuum is just as effective (or ineffective) as oxygen, is derived from such experiments as those of Bottomley (see also von Zahn, &c.) to the effect that the Volta force continues unchanged in a vacuum : that an alteration of the *metals* affects its value largely, but that a change of the surrounding *medium* does not matter, unless it actually corrodes the metals and spoils them.

But this evidence derived from experiments on vacua has never seemed to me conclusive, because nothing like a real vacuum is ever attained, and even if it were, it is known with what surprising tenacity ancient air-films cling to solid surfaces ; the gaseous substance within molecular range of the solid substance being almost a part of it and not readily changed. It clings by cohesion, just as the parts of the solid substance itself cling. It is subject to Laplace's K, enormous molecular pressure. Mere exhaustion, lessening the pressure by one atmosphere, hardly disturbs it.

It was the extreme difficulty of making experiments in vacuum and substituted-media crucial that long ago deterred me from attempting them. Mr. J. Brown attempted some * ; and now fortunately Mr. Spiers has made a brave and distinctly successful attempt in the same direction, an attempt that will, I hope, be persisted in †.

That the free or bounding surface of the metal has something to do with the Volta effect, at least in modifying its value, is proved not only by the long-known observations, say, of Ayrton & Perry, of Pellat and others, on the effect of corrosion and oxide films, but also by the interesting experiments of Mr. Erskine Murray on burnishing ‡. Simple burnishing of the parts *not* in contact can run the Volta force up considerably, from ·7 volt to 1·02 volt in a certain instance ;

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* Proc. Roy. Soc. vol. lxiv. p. 369 ; see also vol. xli. p. 294, and Phil. Mag. 1878, 1879, and 1881.

† Phil. Mag. January 1900.

‡ Proc. Roy. Soc. vol. lxiii. p. 113.

and scratching drops it again*. But these surface-effects are admitted by Lord Kelvin, and are not thought to be even indirectly concerned with the zinc-copper junction and the contact-force there located†. I should say that so great a variation, caused by a slight change of surface, shows that there is something already going on at the metal-air surface to vary. I am not aware of anything that can be done to a metal-metal junction that will affect the Volta force—except of course heating it. Lord Kelvin, however, would say, I suppose, something like this:—In a simple Volta electrostatic arrangement there are three boundaries, zinc/copper, copper/æther, æther/zinc, and there is a contact-force at each. The Volta effect observed is the sum of the three. Its seat is mainly at the zinc-copper junction; it is due to the attraction of the two metals for each other, and its value is calculable approximately from their energy of combination. The effect of any contact-force there may be at the other boundaries is to modify the observed magnitude of this true and chief Volta force. The Volta force also varies in a subordinate manner with temperature, and hence there is a minute reversible Peltier evolution of heat at the zinc-copper junction whenever a current passes. [*End of hypothetical quotation.*]

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* To this I should like to add that the gigantic differences of potential caused by the contact and separation of insulators, or of a metal and an insulator, *e. g.* the contact and separation of mercury or tin amalgam and glass, are very familiar; and the great change, sometimes even of sign, caused in this potential-difference by a modification of surface, for instance by using glass whose smooth or burnished surface has been ground with sand-paper, is well known, and inevitably suggests some cause, whatever it may be, akin to that which causes a less violent but somewhat similar drop of position in a volta series when a burnished surface of zinc is scratched with sand-paper.

† The following quotation from Lord Kelvin's Royal Institution Lecture may be made:—The result of the burnishing experiments "shows that the potential in zinc (uniform throughout the homogeneous interior) increases from the interior through the thin surface-layer of a portion of its surface affected by the crushing of the burnisher, more by ·32 volt than through any thin surface-layer of portions of its surface left as polished and scratched by glass-paper." If I may say so, I should express this fact in exactly the same way, viz. that the natural potential-difference between clean scratched zinc and dry air can be increased one third of a volt by burnishing its surface with a steel tool. (A remarkable fact and one not easy to explain). But I should not go on, as the next sentence goes on:—"The difference of potentials of copper and zinc across an interface of contact between them is only about $2\frac{1}{2}$ times the difference of potential thus proved to be produced between the homogeneous interior of the zinc and its free surface, by the burnishing."

Size of Atoms.

The doctrine of Lord Kelvin about the energy of attraction of plates of molecular thinness approaching each other to within molecular distance and so virtually forming an alloy, though admirably ingenious, proves as it seems to me too much, *i.e.* gives too sharp an upper limit to molecular dimensions; for, as he shows with great clearness in a table in his Royal Institution discourse already often quoted, the estimate of 10^{-9} cm. for molecular thinness and distance would cause the combining metals to rise to a temperature of 7900° C., or more than the probable temperature of the sun! Yet there is nothing out of the way in a molecular estimate of 10^{-9}. On the other hand, an estimate of 10^{-8} yields a rise of temperature of 79°, which appears to agree very well with the order of magnitude (36° Roberts-Austen, 77° Dr. Galt) obtained in actual experiments on the heat of formation of a zinc-copper alloy, a truly remarkable coincidence. One, however, that would be spoilt if the molecular-dimensions' estimate were only *halved*, for the theoretical rise would then be over 300°.

With deference I submit that the air-films, with which the metals employed in ordinary voltaic experiments are certainly coated, ought to be left on them for the data to be applicable; and in that case, when the molecular approach is made, the metals are not so much alloyed as *burnt*; so that a rise of temperature of several hundred degrees is reasonable, and a corresponding molecular estimate of say half 10^{-8} is also reasonable and likely. But in the metallurgical making of brass it is not to be supposed that the metals entering into combination are coated with air-films of any importance, for their proportion of free surface is insignificantly small. Hence I think the Volta effect has nothing really to do with the making of brass.

To carry out the above combustion process, that is the voltaic approach of metallic foil of molecular thickness and its investing oxygen coat, it is not necessary to complicate matters by using *two* metals; and in the Phil. Mag. for May 1885, p. 364, I endeavoured to make a somewhat precise estimate of molecular magnitudes in this way, and even to discriminate between the molecular dimensions of different metals, since x comes out proportional to the square root of the atomic weight divided by the square root of the density and multiplied by the square root of the heat of oxidation.

Chapter III.

Statement of the present condition of the Controversy.

The opposing sides of the old controversy used to be called contact theorists and chemical theorists. If this were ever a correct designation it is not the correct designation now.

There is an E.M.F. at a junction of two media, and this may be called the E.M.F. of contact, without any view as to its origin or magnitude.

This contact E.M.F. may be caused in a chemical or in a physical manner. It is generally admitted, I believe, that the E.M.F.s concerned in thermoelectricity are caused in a physical manner. It is generally admitted, I believe (I think the statement will not be objected to in substance though its purposely crude wording may be criticised), that the E.M.F.s concerned in Volta contact electricity, as well as in ordinary voltaic electricity, are caused in a chemical manner. In saying this I am not intending any controversy, I am only trying to state. The best plan perhaps at this stage is to be more explicit.

I hold that Volta forces can be calculated, as regards their major part, from the differential energy of combination of the metals with oxygen (or other active surrounding element), and I have justified this, more or less completely, by numerical calculations (B. A. Report, 1884; Phil. Mag. April 1885, § 17, pp. 272, 274, &c.) based upon the great fundamental voltaic-cell paper of Lord Kelvin in 1851.

Lord Kelvin, on the other hand, holds that the Volta force can be calculated, as regards its major part, from the chemical affinity of metals for each other; or, to be specific, from the energy of combination of zinc with copper in the formation of brass. It is true that for the calculation to be made in this order, an estimate of molecular dimensions must be postulated, whereas his original calculation treated the order of calculation inversely; but this is of no immediate consequence, and no one at the present date has any serious compunction at including the order of ordinary molecular dimensions among data practically known.

Very well then, unless this statement be objected to, I say that the opposite camps are involved both of them in contact views, and both of them in chemical views. It is not a question of whether physical contact or some form of chemical action is operative; it is a question of which of several contacts is the really effective one, and what kind of chemical action or chemical affinity is the active cause.

Is it the contact and the chemical affinity across the metal-metal junctions, or is it the contact and chemical affinity across the metal-air junctions?

The opposite camps are thus metallic versus dielectric.

I say oxygen. Lord Kelvin scouts oxygen and says brass. He also says æther, and I am willing to say æther, too, in some sense later on, if the evidence permits; but meanwhile, it is more commonplace and safer to say oxygen: for undoubtedly oxygen is there.

Lord Kelvin does not deny the possibility, perhaps the probability, of *some* E.M.F. at the metal-air or metal-vacuum junction, which contributes to the total Volta effect, but I apprehend that he does not believe its contribution to be great. Nor, on the other hand, do I deny the existence of an E.M.F. at the metal-metal junction, which again contributes to the total observed Volta effect, but I assert that we know its contribution to be small.

How big it is in my opinion is answered above in Chapter I. It is measured by the Peltier effect (Profs. Ayrton & Perry will here ejaculate, Stuff and nonsense! and Lord Kelvin will support them. R. I. Discourse, §§ 23 & 24.) The metal-air force is of the order volts. The metal-metal force is of the order millivolts.

Not much is known for certain about the Peltier or physical forces at metal-liquid or liquid-liquid junctions, and they are difficult to measure; but they have been partially measured by Bosscha and by Bouty (see reference in my Report, p. 189, Phil. Mag., March 1885). They may also be theoretically estimated in the way suggested by Dr. Hopkinson in the Phil. Mag. for October 1885. M. Bouty thinks that he has shown that the relation $\Pi = \mathrm{T}d\mathrm{E}/dt$ holds at such junctions. What is certain is that if all the Peltier forces are added algebraically together in a complete circuit at uniform temperature, then, whether the completion be dielectric or electrolytic, $\Sigma(\Pi) = \mathrm{T}d\mathrm{E}/dt$; as Lord Kelvin and von Helmholtz have proved, for the two cases of (1) dielectric medium, (2) electrolytic medium, respectively.

Thus the difference or controversy is no longer, if ever, a difference between contact and chemical action; a chemical contact seems to be admitted now by both sides, but there is an essential and by no means a nominal difference on the question of the localisation both of the E.M.F. and of the chemical contact. I locate the Volta force (the chief part of it) and the chemical contact too, at the air boundary of each metal. Anything occurring at the metallic junction I regard as physical. Lord Kelvin locates the chief part of the Volta force at what he is able to regard as an effectively chemical contact, the zinc-copper junction; and I presume that he regards whatever happens at the metal-æther boundary as physical.

If asked why I maintain the zinc-copper junction to be chemically inert, I pass a current across it, and point to the absence of any chemical change there. If I am chaffed for over-veneration for oxygen and its nascent or potential effect on metallic surfaces, I again pass a current, by whatever means are possible, and show oxide (or more likely sulphate, this acid radical having much the same differential energy of combination with zinc and copper as oxygen has. Nor is that of chlorine very different. But one can show oxide itself if pressed, by using a lead electrode, or a copper one with an intense current).

But if told that this cannot happen always, and that the energy of combination with something (say sulphur) must be very different, I fully admit it; but then I say that in an atmosphere of which the active ingredient is sulphur (say sulphuretted hydrogen) the Volta force will be different too. Mr. J. Brown [*] has shown that it is, but the conclusiveness of the experiment is evaded by pointing to films of sulphide which introduce fresh contact-forces and complicate the circuit.

So here begins a conflict of experimental testimony and interpretation. Lord Kelvin depends on the experiments of Mr. Bottomley in a hydrogen vacuum [†]. I am now able to appeal to the still more elaborate and to me satisfactory experiments of Mr. Spiers (Phil. Mag. Jan. 1900). In so far as they are not conclusive, and I must assume that they are not yet rigorously conclusive, they should be repeated and improved. The research is bound to be laborious and troublesome if properly executed. I will only say, in case any young and energetic experimenter takes the matter up, that Mr. Spiers seems to me in method and motive extremely on the right track.

The question of Expression in terms of Potential.

Superposed upon the controversy as to the junction at which the main contact force really exists, there has arisen another controversy, chiefly concerned with words or modes of expression, concerning the most convenient method of defining the potential of a conductor, and especially the difference of potential between two metals.

It has been customary with certain writers, among them Professor Perry, to define the potential of a conductor as the potential of a point in the air near it,—the work that must be done to convey unit electric charge from the earth (or any place of zero potential) to a point very near the conductor; or, better, to a point in a hollow surrounded by the conductor.

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[*] Phil. Mag. August 1878 *et seq.*

[†] Mr. Bottomley sums up thus (British Association Report, 1885, pp. 901–903):—"The result of my investigation, so far as it has gone, is that the Volta contact-effect, so long as the plates are clean, is exactly the same in common air, in a high vacuum, in hydrogen at small and full pressure, and in oxygen. My apparatus, and the method of working during these experiments, was so sensitive, that I should certainly have detected a variation of 1 per cent. in the value of the Volta contact-effect, if such a variation had presented itself."

I have never been able to see why these philosophers hesitate to complete the process and give the charge actually to the conductor. Why do they stop short outside? The completion of the process is so easy that precaution is needed to avoid it.

It is usually an easier matter to measure experimentally the potential of a conductor, a thing which can be connected directly by a wire to an electrometer, than it is to measure the potential of a point in air or other insulator; the latter operation requiring a water-dropper or a smoking match or an infinitely sharp point.

It has been authoritatively stated that the heterogeneous molecular structure of a metal makes it difficult to affix any meaning to the potential of an inaccessible point inside it; but if this difficulty were a real one it would surely apply still more forcibly to a heterogeneous molecular insulator. The difficulty, however, seems to me purely imaginary from any practical point of view; we need have nothing to do with the molecular structure of a metal in this connexion; by hypothesis it is a conductor, its molecules are all effectively connected, and the potential of one point is the potential of all. Nothing can be simpler than the statement that in electrostatics every part of a conductor is at one potential. We need not put on what Lord Kelvin has somewhere called a molecular microscopic binocular, and examine the atoms on all occasions.

If asked to *define* the potential of a metal, with reference to some arbitrary standard conductor given as zero, I have only to say—the work needed to transfer a small unit charge from one to the other: or the potential energy of each unit of charge existing on the metal, provided the removal of that charge does not appreciably affect the potential: or, better, dW/dQ. Where is the difficulty? The process of charging a conductor is experimentally easy, why not introduce the process into the definition *.

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* Nevertheless, Lord Kelvin says:—"There has been much of wordy warfare regarding potential in a metal, but none of the combatants has ever told us what he means by the expression. In fact, the only definition of electric potential hitherto given has been for vacuum or air or other fluid insulator. Conceivable molecular theories of electricity within

If the potential of a metal is high, positive electricity tends to flow away from it or out of it, and does flow if a path free from obstruction is provided. If the potential of a metal is low, positive electricity tends to flow into it.

That the potential of an isolated piece of zinc is lower than the potential of an isolated piece of copper is proved (I hold) by the undoubted fact that a rush of electricity takes place from one to the other directly they are put into contact. The electricity is driven by the difference of potential: the metals may be brought near and facing each other so as to constitute the plates of a condenser of appreciable capacity; then let them touch, and the flow automatically occurs. If potential is that which determines electrical transfer, if it be the property whose gradient is electromotive intensity, the natural statement about the previous potential of the two metals is obvious. Before contact they were at different potentials; while they are in contact they are at the same potential. The difference of potentials is due to the unequal atomic forces straining at their frontier; the equality of potentials is caused by the equalising electric transfer, *i. e.* to the production of charges which hold the still existing chemical forces in equilibrium. What can be simpler than this mode of expression?

The other mode of expression says that the metals in contact are at different potentials; meaning that the air near each is at a different potential. If that is the meaning, why not say so? It is an undoubted fact. The step of potential in the air is experimentally demonstrable, the only question concerns the step of potential across the junction of the two metals.

To transfer a unit charge from copper to zinc in contact involves no appreciable work, whether it goes through the

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a solid or liquid conductor might admit the term potential at a point in the interior; but the function so called would vary excessively in intermolecular space," &c. (Footnote to R. I. discourse, p. 13.)

He goes on, however, "It would also vary intensely from point to point in the ether or air outside the metal at distances from the frontier small or moderate in comparison with the distance from molecule to molecule in the metal." And with this sentence I can quite agree; as well as with the bare fact stated at the end of the previous sentence.

junction or whether it goes out and through the air[*]. To transfer electricity from *near* the copper to near the zinc involves a definite amount of work, provided that by "near" we do not mean within molecular range; and it requires the same amount of work whether we carry it through the dielectric, or whether we plunge it into the copper and then pull it out of the zinc. If this statement of fact be not disagreed with, it is surely more convenient to say that the zinc and copper in contact are at the same potential, and that the air or space in their immediate but not molecular neighbourhood differs in potential[†]. In other words, that there is a sudden step of potential in crossing the frontier from metal to air, a step which I have reckoned as about 1·8 volts up out of zinc, and about ·8 volt up out of copper, and so a (roughly speaking) 1 volt gradual descent of potential in the air or space near them.

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[*] I think this is the clearest form of statement. It is possible to say there is a cyclical E.M.F. round a circuit like this with two different paths, and that the resultant force is opposed by air resistance; but when the gradient of potential in the air is taken into account as part of the E.M.F., there is equilibrium, and the cyclical E.M.F. is zero. It is merely a question as to which is the most convenient form of expression; there is no controversy in it: the question is touched on again at the end of the next footnote. All that I require for my purpose is the admission that no appreciable work is needed to transfer electricity across the copper-zinc junction; while work is needed to transfer it in the air from near the copper to near the zinc.

[†] It may be permissible to quote a sentence from Dr. John Hopkinson's contribution to the discussion on the same subject at the Institution of Electrical Engineers (Journal, 1885, p. 235) :—"Professor Perry defines the difference of potential between a piece of copper and a piece of zinc to be the energy required to transfer a unit of electricity from near the copper to near the zinc through the dielectric. On the other hand, as I understand the matter, Dr. Lodge, and probably Clerk Maxwell, define the difference of potential to be the energy required to transfer a current of electricity from the copper to the zinc through the junction between the copper and the zinc. Now, it appears to me that Dr. Lodge has very clearly shown that his way of looking at the matter is the more convenient; for, in the first place, it expresses, with the greatest ease, all facts that have been observed. When copper and zinc are in contact with air there is a difference of potential at the three junctions, and the sum of the three differences of potential is not equal to zero; and we have no difficulty in explaining all the electrostatic effects that we have obtained. Dr. Lodge has so clearly proved the convenience of his way of looking at the matter that it would be only wasting your time if I were to attempt to reproduce his arguments. It seems to me better to take that basis and pursue it. Now, if we take that basis as our starting-point, it is very easy to set forth all the theory of thermoelectricity, and the formulæ given at the end of Clerk Maxwell's chapter on that subject can be proved with the greatest ease; it is also easy to extend these formulæ to the case in

I have found in the reported discussion at the Electrical Engineers (Journ. Inst. E. E., 1885, vol. xiv. p. 233) the following ingenious and evidently careful note added later by Prof. Perry. I will first quote it, and then paraphrase it into what I consider greater simplicity of form:—

"To be quite correct, let what I have called 'tension' in a metal *a*, at the absolute temperature *t*, be denoted by ${}_tP_a$; and the increase of potential from *a* to a metal *b*, as measured inductively, by ${}_tV_{ab}$, then the electromotive force of a thermo-electric circuit of two metals, *a* and *b*, whose junctions are at temperatures t_1 and t_2, is

$$E = {}_{t_2}V_{ab} - {}_{t_1}V_{ab}.$$

The Peltier effect at a junction is

$${}_t\Pi_{ab} = {}_tP_b - {}_tP_a - {}_tV_{ab},$$

where

$${}_tV_{ab} = (k_b - k_a)t\left\{T_{ab} - \tfrac{1}{2}t\right\} + C_b - C_a,$$

$${}_tP_a = \tfrac{1}{2}k_a t^2 + C_a.$$

k_a and C_a are constants peculiar to the metal *a*, and T_{ab} is a constant peculiar to the two metals *a* and *b*.

Hence

$${}_t\Pi_{ab} = t \cdot \frac{d}{dt} \cdot {}_tV_{ab},$$

or the Peltier effect is proportional to the absolute temperature and to the rate of change of the contact-force with temperature."

So far the quotation; now for its interpretation.

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which we have chemical action going on, and to foreshadow the precise method by which we may be able to ascertain exactly what the difference of potential is between copper or zinc or other metals and electrolytes."

He then makes some further remarks of considerable interest which were expanded by him later in the Phil. Mag. for October 1885. All I would add to the above admirable statement is that the emphasis required is upon the word "near" in the 3rd & 4th lines, and that the immediately following specification of path—"through the dielectric"—is not really essential. The potential-difference is independent of path in this case. Replacement of dielectric by electrolyte, unable to stand the potential-gradient statically, may be said to destroy equilibrium and yield a cyclical E.M.F. and a current; but, strictly speaking, the cyclical potential-difference is still zero, when resistance to steady current is taken into account; always zero, in fact, even within the variable stage, when acceleration-reaction or self-induction is likewise included.

Paraphrase :—Let the step of potential from inner metal to outer air across the boundary film be p, and let it be a function of temperature such that

$$p=m+\tfrac{1}{2}kt^2. \quad \text{[Assumption.]}$$

Let the change of potential from air near metal a to air near metal b be V_{ab} or V ; it follows that this also will be a function of the temperature. Because, if Π be the E.M.F. located at a junction of the two metals, the total change of potential on a journey all round from a to b and back, out *via* the air and back *via* the junction, is zero ; or

$$p_a+V_{ab}-p_b+\Pi_{ba}=0.$$

[This is only a roundabout way of saying that the Volta effect is the sum of the three junction-forces.]

Further, if we construct a complete circuit of the two metals and keep their junctions at t_1 and t_2 respectively, and then travel right round outside the circuit, keeping in the air near the metals, we shall encounter an E.M.F.,

$$E=V_1-V_2.$$

[Here again there is an assumption :— viz. that the Thomson force in a metal bar, with its ends kept unequally hot, will show itself outside not as a slight gradient of potential in the air along and near the rod, but as a slight modification by temperature of the step of potential in its boundary film. This assumption is therefore quite consistent with the one made just above, $p=m+\frac{1}{2}kt^2$.]

Further, let us assume that $\Pi=(k_a-k_b)t(t_0-t)$; then it follows by common algebra that

$$\Pi/t=dV/dt.$$

So with all these assumptions, and all this needless and artificial attention to external occurrences, nothing is obtained beyond the admitted laws of the closed thermoelectric circuit, most simply written thus :—

$$\Pi=tf'(t) ; \qquad E=f(t_1)-f(t_2).$$

See, for instance, my footnote to p. 270 of Phil. Mag. for March 1886, or see pp. 265, 266 of the same paper.

I trust that I have made it clear that I do not regard this matter of the definition of potential as of the same importance as the seat of E.M.F. in the pile. In no other part of this paper have I paid any attention to the wording of propositions in terms of potential ; it is a subsidiary dispute superposed on the main disagreement, which latter is in no sense a matter of words or definition.

Nevertheless the two disputes are somewhat closely allied, and the clarification of one ought to result in pacification of the other.

Chapter IV.

My advocated mode of regarding the Mechanism of the Chemical Contact Force.

I have elsewhere tried to explain the mode in which I suppose the oxygen to act to bring about that momentary transfer of electricity which occurs across the junction of two metals the instant they are put into contact. The facts postulated are (1) the fact of chemical affinity between oxygen and metal, of amount different for different metals, and (2) the fact that oxygen atoms are, at any rate some of them, negatively charged.

On the strength of these facts I see a surrounding layer of straining oxygen atoms seeking to move up to the zinc, but unable to do so because of "the impossibility of conferring an absolute charge on matter," as Faraday in his ice-pail experiment put it, or because of the "incompressibility of electricity," or because there is no avenue for the supply of electricity of opposite sign. Consequently we have a state of siege, a kind of incipient polarisation, but no charge. The zinc is somewhat in the condition of an insulated sphere surrounded by a concentric negatively charged shell, so far as the interior of the shell is concerned: outside the conditions are different. And the cause of the stress is different: there are no lines of electric force, there is no *electrical* difference of potential; whatever force or potential-difference exists between isolated zinc and air is chemical in its nature—the result of chemical affinity. The force may be due, as Helmholtz puts it, to a specific attraction of zinc for electricity, or it may be due to a specific attraction for oxygen; but to whatever it is due, so long as the surface is homogeneous, it is inoperative, it results in no energy transformation or work done, it is a deadlock.

Now establish connexion at one point with some neutral substance, say platinum, or a less strained-at substance, like copper; instantly an avenue for the relief of the strain is provided, positive electricity flows across the junction into the zinc, takes up its abode on the surface facing the oxygen atoms, the oxygen atoms approach slightly nearer all round, the surrounding molecules all round are polarised, their negative poles inwards, their positive poles outwards, a double layer is set up on the zinc, and lines of force appear all through the surrounding dielectric. These lines reach from the zinc free-surface to the copper free-surface, distributing themselves according to the ordinary rules of electrostatic capacity, and their terminations on the copper constitute its negative charge. In other words, the oxygen atoms are slightly further removed than before from the copper, and it is to that extent protected even from its previous small tendency to oxidation ; on the other hand, the oxygen atoms have approached slightly nearer to the zinc. Thus my doctrine is not a doctrine of chemical combination, but of chemical approach. The oxygen atoms approach nearer the zinc, recede further from the copper, and by these slight motions produce the whole Volta effect.

But this it may be said is nothing but a voltaic cell, except that the electrolyte is replaced by a dielectric, and so the current is momentary, not continuous. Precisely, that is my meaning.

But then, it will be objected, if a current did pass, there would be actual oxidation ; since for every electric unit that passes in a cell there must be an electrochemical equivalent of zinc oxidised. To this I agree.

Well then, pursues the objector, consider a condenser of great capacity with its alternate plates made of zinc and copper, very close together, and then short-circuit it at some point ; there will instantly be a great flow of electricity across the junction to charge the condenser, and accordingly there will be a perceptible amount of zinc oxidised. Your mere approach of oxygen atoms without combination will no longer serve.

At this point I appeal to arithmetic. The charge on an atom is of the order 10^{-11} electrostatic units. The oxygen atoms immediately in so-called contact with the zinc are constituents of its condensed air-film, a film so dense as to be virtually a liquid, since it is subject to the intense molecular pressure. Not really a liquid, because it is far above the critical point, but not perceptibly differing from a liquid in density. If this be objected to, it is not essential to my argument, because there is plenty of margin; only it seems to me likely to correspond roughly with the truth. The number of atoms per square centimetre in the layer facing the zinc will therefore be of the order 10^{16}. Of these only a portion will be oxygen; and probably it may be said that only a small proportion are ionised and so open to combination. But as I do not need combination, I see no necessity to postulate ionisation, or to care what proportion are in this condition. Certainly I need molecules capable of being polarised electrically, but that at the present date will hardly be denied to any material molecules whatever.

Very well then, if for any reason polarisation takes place, the surface-density of the charge on either face of the double layer can be $10^{16} \times 10^{-11} = \sigma = 10^5$ electrostatic units per square centimetre, at a maximum. The mechanical tension across the layer is $2\pi\sigma^2$, and the intensity of electric field there is $4\pi\sigma$, which is also the gradient of electric potential.

Now the thickness of the layer is of molecular dimensions, 10^{-8} centim. say; hence the difference of potential between its faces, that is the difference of potential between the zinc and the air in its neighbourhood, is $4\pi\sigma z$, which is of the order $(12 \times 10^5 \times 10^{-8} = 10^{-2})$, one-hundredth of an electrostatic unit, or 3 volts. Now plainly this is of the right order of magnitude. The Volta effect observed *can* be explained by such an electrical double layer, by such a chemical layer of straining oxygen atoms, at a metallic surface *.

That it can be equally well explained for metals in absolute vacuum or free æther I would not presume to deny; but I cannot do the arithmetic for that case, because of an utter lack of data. It is to be observed, however, that the only gaseous or material substance needed (other than metal) is the coherent film on the surface; all the rest of the gas is merely a dielectric medium for the transmission of electrostatic induction or lines of force, and for this function an absolute vacuum serves perfectly. Consequently, merely removing the plates into the receiver of an air-pump will make no practical difference.

But still, so far, I have not met the hypothetically suggested difficulty about the condenser of large capacity and the amount of real chemical action needed to account for the current required to charge it to the voltaic difference of potential.

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* See also a footnote to p. 379 of a paper in the Phil. Mag. for October 1885, where I reckoned practically the same thing.

We have only to proceed with the calculation.

The condenser formed by the opposing surfaces of zinc and copper is a condenser of the same (or comparable) area to that molecular condenser just postulated between either metal and the air. The only difference is that these last are of molecular thinness, whereas the condenser formed by well-fitting plates of zinc and copper is of a moderate thinness, z, say the hundredth part of a millimetre, or something of that order.

Hence, when the plates are approached from infinity to this distance z, and are put into contact to establish the state of polarisation, there will be a rush of charge out of the molecular condensers into the newly formed condenser; for they are condensers in series, and every unit gained by one must be lost by the other.

But since the molecular condensers are to retain their original potential-difference, this supply of electricity can only be given by a change in capacity, *i. e.* a change in their molecular thickness x, such that

$$-\frac{dx}{x^2}=\frac{1}{\infty}-\frac{1}{z},$$

or

$$dx=\frac{x^2}{z}=\frac{10^{-16}}{10^{-3}}=10^{-13}\text{ cm.},$$

the hundred-thousandth part of molecular magnitude.

Thus the diminution in thickness of the superficial double layer, or the approach of the oxygen atoms, in an extreme case, has only to be a hundred-thousandth part of their whole distance. This can hardly be called chemical combination: indeed it is a scarcely perceptible chemical *approach.*

Put in another way it amounts to this: that if the oxygen atoms varied their distance from the zinc and the copper respectively (one decreasing, the other increasing) by so much as a tenth of 1 per cent., the electricity so set free or transferred from one surface to the other would be able to charge an ordinary condenser of the same area in the intervening space to a density of 100 C.G.S.; which is considerably more than ordinary air can stand.

The only way to get a perceptible amount of real oxidation, that is an approach over the whole molecular distance, is either to bring the condenser plates themselves within molecular distance of each other, which would squeeze out the films and modify the whole action, or else to bring them within molecular distance of different parts of one and the same liquid conductor (so that the whole strain is thrown upon the molecular film-condensers and none upon any intervening material); and this is exactly what is done in an ordinary voltaic cell.

CHAPTER V.

Osmotic Pressure or Diffusion View of a Voltaic Cell.

The osmotic pressure hypothesis, strictly speaking, perhaps hardly belongs to my present subject, since whatever controversy or question has gathered round it is of a different kind from that concerning the seat of the E.M.F. The osmotic pressure hypothesis does not concern itself apparently with the Volta electrostatic effect, but with the mechanism of propulsion in a voltaic cell: it hardly cares to discriminate between the two cases, for they appear in many respects much the same; and it locates the seat of the E.M.F. quite definitely at a junction on one side of which at least there is a liquid, or substance with loco-mobile atoms, and not at a metal-metal junction: it deals entirely with moving ions, such as cannot exist in true solids. Moreover it is not a hypothesis really distinct from that of the recognized chemical combination associated with a current-producing cell, only it regards that chemical combination from a different point of view—from the dissociation or ionisation point of view. Instead of saying that zinc is oxidised or that zinc sulphate is formed, it professes to regard atoms of zinc as shot off into the liquid in a non-combined or free form: ultimately, no doubt, to enter into real combination, but existing for a time, and always in a certain proportion, in the form of practically free ions. Thus the full discussion of the osmotic pressure hypothesis is essentially chemical in its nature, and need not here concern us. At the same time so many people are interested just now in this remarkable view of chemical combination, that I refrain from passing it by altogether; though, as it is not a hypothesis specially and long familiar to me, my remarks on it will not have any particular weight. Fortunately there are several writings to which a student of such matters can be referred—the treatise of van t' Hoff, the work of Arrhenius and of Planck, and the textbooks of Ostwald and of Nernst, especially of Nernst; and likewise the excellent Report on these subjects presented to the British Association in 1897 at Toronto by Mr. W. C. D. Whetham, as well as to his book on 'Solution.' Furthermore, I may refer to the works of Dr. J. Larmor, especially Phil. Trans. vol. cxc. p. 270; and to a paper by Prof. Poynting in Phil. Mag. vol. xlii. p. 289 (1896), where it is shown that the dissociation hypothesis need not be pressed too literally, that solution may be a kind of chemical combination, and yet that all the facts deduced on the free ionisation hypothesis can be true. This compromise is, however, criticised by Dr. Larmor in a footnote to page 273, *op. cit.*; and Boltzmann is able to regard osmotic pressure as due to a true molecular bombardment, seeing that in the liquid state the molecular velocities should be the same as in the gaseous state at the same temperature, the mean free paths alone being smaller. On the other hand, it has been frequently claimed that any extension of gaseous laws, *i. e.* of laws deduced from the collisions of free particles, to the extremely hampered condition of a liquid, where the particles are always within each other's molecular range, must be illegitimate.

Without attempting to decide these moot points, we will here consider the question open whether the statement in terms of free ions is only a mode of expression, or whether it corresponds with the real facts; corresponds with them, that is to say, not only in result, but in actual detail. Prof. Poynting's paper, for instance, does not decide against the latter possibility, it only attempts to show that it is not really *necessary* to grant free ions as a physical reality; but Mr. Whetham evidently inclines to the idea that they are at least free of each other, and adduces an argument in favour of that view (pp. 233, 244, B. A. Report 1897) which is worthy of attention. But, while assuming that opposite ions are free of each other, he considers that they are both attached to the solvent, and are by no means really and bombardingly free, as are the molecules of gases. Prof. Poynting appears to agree *; but, as said above, the agreement is not universal.

The most successful application of Nernst's theory is to the calculation of the feeble E.M.F. of cells consisting of one metal but two liquids, especially when the two liquids differ only in concentration of one and the same salt.

The ideas underlying all such calculations are (*a*) that the ions migrate for two reasons: one their own random motion whereby they naturally diffuse on the average from the more concentrated to the less concentrated solution, carrying their charges with them, the other an organized motion caused by the propulsive influence on these same charges of the gradient of potential caused by their gradual diffusive accumulation; and (*b*) that in the steady state ultimately attained the rate of migration of opposite ions must become equal: otherwise the liquid would be constantly altering its composition in places.

Indeed the fact that equivalent quantities of anions and cations are liberated at the electrodes, combined with the definiteness of ionic charge, shows that in electrolysis the resultant effective velocities of anion and cation substance relatively to the electrodes are equal †.

Consider now the charged atoms or ions in a cylindrical space of volume $A dx$, with n of them in each unit of volume.

Let them be subject to an applied potential gradient dV/dx, and also to a self-excited osmotic pressure gradient dp/dx; then if e is the charge on each atom, the electrical force it experiences is

$$e\frac{dV}{dx},$$

while the mechanical or osmotic force it experiences is the whole pressure difference on the element shared among the total number of atoms, which is

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* Nature, 1896, vol. liv. p. 571; vol. lv. pp. 33, 78, 150, &c.

† This statement seems to require a word of explanation or expansion. So much stress has been laid upon the fact of different intrinsic velocities of opposite ions when under the same conditions, that it is apt to be forgotten that in ordinary electrolysis the conditions are such as to force equal, or at least electrically equivalent velocities, on anion and cation substance taken as a whole, in the steady state. The ions are propelled not by outside forces acting from the electrodes, but by internal actions: the readjustment of the whole material must be attended to. The intrinsic speed of a projectile is greater than that of the gun-recoil, yet, after a battery has fired, the centre of gravity of the whole is no nearer the

$$\frac{\mathrm{A}dp}{n\mathrm{A}dx} \quad \text{or} \quad \frac{1}{n}\frac{dp}{dx}.$$

This latter mechanical force acts equally on anions and cations, but the electrical force acts oppositely on each set; so the total force on the one set is the sum, on the other set is the difference, of these two forces. If u_1 and v_1 are the usual migration constants representing the velocities of anion and cation respectively under unit potential gradient, their velocities under unit force will be u_1/e and v_1/e, and the actual velocities under the above forces can easily be written down. But the actual velocities in the steady state will be equal; therefore, as the condition of steadiness,

$$\frac{u_1}{e}\left(\frac{1}{n}\frac{dp}{dx}+e\frac{d\mathrm{V}}{dx}\right)=\frac{v_1}{e}\left(\frac{1}{n}\frac{dp}{dx}-e\frac{d\mathrm{V}}{dx}\right)$$

which simplifies to

$$ne\frac{d\mathrm{V}}{dx}=\frac{v_1-u_1}{v_1+u_1}\frac{dp}{dx}.$$

At this stage it is customary to introduce the osmotic pressure gas-analogy, writing the characteristic equation of a mass M and volume V,

$$p\mathrm{V}=\mathrm{MRT},$$

where R is a characteristic constant, viz. the specific heat of expansion per gramme of perfect gas, which for hydrogen is accidentally almost equal to J, the specific heat of water.

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target than before. The mass-speeds are equal and opposite. In the electrical case the charge-speeds are equal and opposite. Direct experiments on specific migration velocity (such as those I described in the Brit. Assoc. Report for 1886, pp. 393, 408) are all made in purposely heterogeneous solutions; so that the motion of specific portions of matter can be discriminated and followed. Even in such heterogeneous liquids the current-strength is the same across every section; but the local potential-gradient depends on the local conductivity, and the concentration is arbitrary: it is still true, however, that the potential-gradient is the same for anion as for cation at any given place; and hence if they do ultimately travel at the same pace in spite of intrinsically different ease of travel, the fact must be expressible as due to an accumulated osmotic pressure-gradient which opposes the quicker and helps the slower.

Writing $\frac{M}{V}=\rho=nm$, and considering the gas pressure p to be the osmotic pressure,

$$dp=m\mathrm{RT}\,dn,$$

at constant temperature.

And so finally the steady difference of potential due to diffusion between two solutions which differ only in concentration, one containing n the other n' active atoms to the litre, is

$$\mathrm{V}-\mathrm{V}'=\frac{m}{e}\,\mathrm{RT}\,\frac{v_1-u_1}{v_1+u_1}\log\frac{n}{n'}.$$

I have written this out fully because it is usually somewhat slurred over, the electrochemical equivalent m/e omitted, the argument rendered obscure, and the dimensions wrong.

It follows that although usually the E.M.F. thus set up is very small, yet by having one of the solutions extremely weak (n' nearly $=0$) the E.M.F. generated may be made surprisingly high, that is a large fraction of a volt; provided the anions and cations concerned do not diffuse at nearly the same rate under the same circumstances.

For instance, if silver is placed in a liquid containing some chloride, no molecules of silver can accumulate in any quantity in the solution, and accordingly the concentration will be almost infinitesimal, and the E.M.F. comparatively high; thus Ostwald gives the following as a cell which has, and ought on his calculation theoretically to have, an E.M.F. of ·51 or ·52 volt.

$$\mathrm{Ag}\mid 0{\cdot}1\ \mathrm{AgNO_3}\mid \mathrm{KNO_3}\mid 1{\cdot}0\ \mathrm{KCl}\mid \mathrm{AgCl}\mid \mathrm{Ag},$$

the KNO_3 being introduced for obvious reasons to prevent precipitation of adjacent solutions, but being without influence on the resultant E.M.F.

To calculate the total E.M.F. of a cell, however, it is necessary to take the other boundaries of the liquid into account. It is useless to complete the circuit by liquid, it must be completed by metals, and in the cases now being considered by one and the same metal. Each metal acts as a wall preventing effective diffusion of one at least of the liquid ions: the cathode prevents the cation from advancing, the anode prevents the anion; whatever else the metals may do will be the same at each end, and so balance. This is I believe the form given by Mr. Whetham to Prof. Nernst's argument.

Hence the total E.M.F of such a cell will be the sum of the three junction-E.M.F.'s, metal/liquid, liquid/liquid, liquid/metal:

$$E = R\epsilon T\left(\frac{u_1 - o}{u_1 + o}\log n + \frac{u_1 - v_1}{u_1 + v_1}\log\frac{n'}{n} + \frac{o - v_1}{o + v_1}\log n'\right)$$

$$= \frac{m}{e}RT\cdot\frac{2v_1}{u_1 + v_1}\log\frac{n}{n'}.$$

There is here, fortunately, no question about an innocent-looking but controversial metal/metal junction.

The remarkable thing about this equation is that the data on the right-hand side are all known, and that therefore E can be calculated in absolute measure.

Thus since the characteristic gas constant R, the absolute specific heat of expansion per gram of perfect gas, varies inversely with m the atomic weight, it follows that Rm is an absolute constant, the same for every substance, or at least only differing by a simple multiple, having twice the value for electrolytic as for undissociated molecular substances; hence we may take its value as double that for, say, hydrogen. For hydrogen $m/e = {\cdot}00010352$ gramme per coulomb, and $R = 41{\cdot}6 \times 10^6$ ergs per gramme degree.

Hence at 15° C.

$$E = 2 \times 4{\cdot}16 \times {\cdot}00010352 \times 288\,\frac{2v}{u+v}\log_e\frac{n}{n'}, \text{ joules per coulomb}$$

$$= \frac{{\cdot}114}{1+r}\log_{10}\frac{n}{n'}\text{ volts,}$$

where r is written for the Hittorfian migration ratio of anion to cation intrinsic velocity u_1/v_1. It is remarkable that nothing is wanted except this migration ratio and the concentration ratio n/n' to calculate in absolute measure the E.M.F. of such a cell, with the same metal at either end.

A table of correspondences between theory and experiment is quoted from Ostwald and Nernst by Whetham in his B. A. Report, and they agree very remarkably indeed when one considers that the numbers are absolute numbers and might have been in error by large quantities.

To illustrate this take a cell with decinormal solution of HCl on one side and centinormal solution on the other, so that the concentration ratio $n/n'=10$:—

For the migration ratio we might take Hittorf's own numbers (which he tabulates in the form $u/(u+v)$ &c.) ; but several more recent and presumably more exact determinations have been made, and it may be convenient to quote here the table of absolute velocities given by Mr. Whetham as embodying the most recent measurements in 1897. As I write them they give the ionic velocity, in mikroms per second, for a potential gradient of 1 volt per centimetre (a mikrom being 10^{-6} metre or 10^{-4} cm., about double the wave-length of green light).

Intrinsic Ionic Velocities.

	u_1.		v_1.
Cl	6·9	K	6·6
I	6·9	Na	4·5
NO_3	6·4	Li	3·6
OH	18·2	H	32·0
$C_2H_3O_2$	3·6	NH_4	6·6
$C_3H_5O_2$	3·3	Ag	5·7

So for HCl the migration ratio is

$$r=\frac{69}{320}=\cdot 216,$$

and hence the theoretical E.M.F. of such a cell as that just above spoken of, with a weak solution of HCl opposed to one ten times weaker and connected by any single metal, is

$$\frac{\cdot 114}{1\cdot 216}\log_{10}10=\cdot 0938 \text{ volt},$$

whereas Nernst gives it as observed at ·0926 volt. A very remarkable agreement when we consider how the above absolute constant $4RTm/e$, which I have reduced on the preceding page to ·114 volt, is constituted.

As another example take a cell containing two strengths of NH_4Cl solution, with the same concentration ratio 10 : 1. In this case

$$r=\frac{69}{66}=1\cdot 045.$$

So

$$E=\frac{\cdot 114}{2\cdot 045}=\cdot 0557 \text{ volt},$$

and Nernst gives it as observed at ·0546.

Once more, take a cell filled with KOH solution 10 : 1 ;

$$r=\frac{182}{66}=2\cdot 76,$$

therefore

$$E=\frac{\cdot 114}{3\cdot 76}=\cdot 0303 \text{ volt},$$

and it is observed at ·0348.

A cell of LiCl gives another example, strength as before decinormal and centinormal, that is ·1 gramme equivalent per litre on one side, and ·01 ditto on the other:

$$r=\frac{69}{36}=1\cdot 925.$$

So

$$E=\frac{\cdot 114}{2\cdot 925}=\cdot 0390 \text{ volt},$$

observed at ·0354.

Here more old-fashioned values for the migration numbers give a result more nearly agreeing with observation.

Another cell where the agreement is not so close is one of caustic soda, NaOH. Nernst quotes one with strengths ·235 gramme equivalents per litre on one side, and ·030 on the other, so that the concentration ratio is 7·83, while the migration ratio is $\frac{182}{45}=4\cdot 05$.

The observed E.M.F. was ·0178 volt, whereas the calculated is

$$\frac{\cdot 114}{5\cdot 05}\log 7\cdot 83=\cdot 0201 \text{ volt}.$$

At least that is what I get, but, as in several other cases, the column of "calculated" given by Nernst does not contain the same numbers as those here obtained. Sometimes they agree with observation better, but sometimes worse.

These agreements, though not perfect, are clearly far and away beyond anything attributable to chance, and they practically substantiate the essential features of Nernst's theory, a theory which seems to me to rank high among rational calculations of this kind. The success of this brilliant concentration theory of batteries with one metal and two liquids, or rather one liquid with different strengths, lends weight to the supplementary suggestions of the same great chemist*, that the E.M.F. of batteries containing one liquid and two metals can likewise be calculated on similar lines. So long as the metals are the same at either side, and only the solutions have to be considered, this diffusion theory clearly represents a great step in the direction of the truth, even if it cannot be asserted at present to be the whole truth.

But when the so-called solution-pressure of a metal itself has to be taken into consideration, the ground becomes less secure and satisfactory.

When zinc dissolves in an acid this hypothesis assumes not that the zinc is eaten away by combination with the acid radical, but that it as it were evaporates into the liquid, giving rise to free zinc ions having a certain osmotic pressure.

If asked why zinc should evaporate any more freely into liquid than into air, it may be answered (as Mr. F. H. Neville suggests), because the great cohesive force, Laplace's K, would resist evaporation into air, but would be far less effective in resisting evaporation into a liquid where the change of density is much less sharply emphasised at the boundary. Hence though a certain repugnance may naturally at first be felt to this evaporation theory, it may turn out a reasonable mode of expressing facts, and it demands careful consideration.

The above mere cohesion consideration would tend, however, to make all liquids too much alike in their solvent influence on metals; the form given to the theory by Mr. Whetham and Prof. Poynting, that the ions though free of each other are chemically attached to the solvent, seems far more plausible, and overcomes many difficulties. On either view the following statements hold good.

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* Meaning either Ostwald or Nernst. I cannot pretend to discriminate the portion belonging to each, and I hope it is not necessary. Both have done admirable work in connexion with this subject. I find that the first theory of concentration batteries, based upon thermodynamic and vapour-tension considerations of a less simple kind than those here quoted, and not depending on any ionisation hypothesis, was given by von Helmholtz in 1878 (Wied. *Ann.* vol. iii. p. 201).

When a metal dissolves in a liquid there is no interchange of ions; cations pass into the liquid, but no anions necessarily pass out of it. Sometimes there is an interchange of cations—one set going in and another set coming out—as when iron displaces copper, or zinc displaces hydrogen. Probably some impurity in the metal, enabling galvanic action to occur, is essential to this process, but that is here not a matter of primary importance.

Consider now a Daniell cell of the simplest theoretical kind:

$$\mathrm{Cu} \mid \mathrm{CuSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{Zn}.$$

As soon as the circuit is completed, zinc goes into solution at one end and copper comes out at the other. The difference between the energy of combination of Zn and Cu with SO_4 gives the whole E.M.F.; since, as is well known, the dE/dt and therefore the $\Sigma(\Pi)$ happen in this case to be practically zero.

But what about the location of the E.M.F.? Leaving on one side the extraordinary contention in favour of the zinc-copper junction, there are three other junctions at which the chief portion of the E.M.F. might be located; and at first sight the liquid/liquid junction at the porous partition seems the most likely. For here it is that the actual exchange of Zn for Cu takes place; and hence it may be said, either heat must here be locally developed or else the energy must be used in propelling the electric current and developing the same quantity of heat elsewhere.

But, as Hopkinson virtually pointed out (p. 341, Phil. Mag. Oct. 1885), this involves the tacit assumption that the metallic ions do all the travelling, while the SO_4 is stationary;—in that case the metallic zinc which goes into solution would at first be merely passed on, and the real energy-production would occur where zinc atoms take the place of copper atoms, viz., at the junction of solutions in the porous partition. After that there is a mere passing on again, though now of copper.

But the migration ratio of the ions is in reality different from this, and the SO_4 is by no means really stationary. As another extreme assumption, suppose that the SO_4 ion did all the travelling; then the zinc sulphate solution is strengthened and the copper sulphate solution is impoverished, and the whole positive energy of combination is at the surface of the zinc, while at the surface of the copper there must be a smaller opposition force corresponding to the tearing of the SO_4 away from the Cu there.

Now this concentration in one compartment and weakening in the other compartment corresponds much more nearly than the first hypothesis does with what is observed, the truth being of course something intermediate between the two extremes. Anions and cations both travel, and so the total E.M.F. is shared in certain proportions between all the junctions: a proportion which can be calculated from a knowledge of the relative rates of migration: though the observations of the true migration-ratios may be complicated by molecular electric endosmose through the porous cell. Indeed, so far as I know at present, the migration velocity of SO_4 has not yet been very well directly determined.

But, although all this is valid on any view as to the nature of solution, the above mode of statement belongs to the old-fashioned view of chemical combination, the notion of metallic solution which was in vogue a few years ago. It may be well to state the matter also in terms of dissociation ideas.

The fashionable method is to think of the solvent as little more than a menstrum for a stream of metallic ions to saunter through. We may think of the zinc ions travelling into the liquid and some copper ions leaving it, the adjustment of the proportion between the free zinc and the freed SO_4 being a matter of subsequent diffusion. The solid zinc has, as it were, a certain vapour-tension or osmotic pressure P, the zinc of the zinc sulphate has a certain less solution-pressure p, less because it is there less concentrated than in the solid. Let there be N molecules per c.c. of solid and only n active molecules per c.c. of liquid, then the steady potential-difference between the solid and the liquid will be given by

$$\frac{dV}{dp} = \frac{1}{ne},$$

for in the present case $\frac{v_1 - u_1}{v_1 + u_1} = 1$, the anions being supposed stationary at that junction, since they cannot diffuse into the metal.

So putting $p=\rho\mathrm{RT}=nm\mathrm{RT}$,
we get

$$d\mathrm{V}=\frac{m}{e}\,.\,\mathrm{RT}\frac{dn}{n};$$

or

$$\mathrm{V}-\mathrm{V}'=\mathrm{R}\epsilon\mathrm{T}\log\frac{\mathrm{N}}{n}=\cdot 114\log_{10}\frac{\mathrm{N}}{n}\text{ volt},$$

as the theoretical difference of potential between a metal and a solution of any one of its salts; ϵ being written for the electrochemical equivalent m/e. Even if it is a foreign salt or an acid the potential-difference should be the same, provided there is equilibrium, *i. e.* no "local action."

Suppose now that one metal, with effective concentration N_1 (active ions per c.c.), dips into a solution of concentration n_1; and that this solution changes abruptly to another strength n_2 of the same solution, the circuit being completed by another metal N_2 dipping into that second solution; then the whole E.M.F. of the cell, on the above hypothesis, is

$$\mathrm{E}=\mathrm{R}\epsilon\mathrm{T}\left(\log\frac{\mathrm{N}_1}{n_1}+\frac{u-v}{u+v}\log\frac{n_1}{n_2}+\log\frac{n_2}{\mathrm{N}_2}\right)$$

$$=\cdot 114\left(\log_{10}\frac{\mathrm{N}_1}{\mathrm{N}_2}+\frac{2v}{u+v}\log_{10}\frac{n_2}{n_1}\right)\text{ volt.}$$

One case of this is the one we have already considered at length, where only one metal is employed, that is, where $\mathrm{N}_1=\mathrm{N}_2$, and the E.M.F. depends wholly on the solutions. The other chief case is the ordinary simple Volta cell, where $n_2=n_1$, and where the theoretical E.M.F. depends solely on the two metals.

But now suppose that the two liquids are different, as well as the two metals; there will now be altogether four ionic velocities and four real or virtual concentrations:—

$$u_1,\ v_1\ ;\quad u_2,\ v_2\ ;\quad n_1,\ n_2\ ;\quad \mathrm{N}_1,\ \mathrm{N}_2.$$

So assuming that each solution acts like vacuum to the other, we have intrinsic velocities u_1 out and v_2 in across the liquid boundary of the first solution, or an E.M.F at that place of

$$\cdot 114 \frac{u_1 - v_2}{u_1 + v_2} \log n_1 \text{ volt};$$

together with

$$\cdot 114 \frac{v_1 - u_2}{v_1 + u_2} \log n_2 \text{ volt}$$

to be added to it, for the same boundary, considered from the point of view of the other solution.

Hence in this case, with two different metals,

$$\frac{\mathrm{E}}{\cdot 114 \text{ volt}} = \log_{10} \frac{\mathrm{N}_1}{\mathrm{N}_2} - \frac{2v_2}{u_1 + v_2} \log_{10} n_1 + \frac{2v_1}{u_2 + v_1} \log_{10} n_2.$$

And the first term is usually the most important. For the special case where $\frac{v_2}{u_1} = \frac{v_1}{u_2} = \frac{1}{r}$, the two last terms reduce to the simple concentration expression already familiar, $\frac{2}{1+r} \log \frac{n_2}{n_1}$. The osmotic pressure ratio n_2/n_1 for the liquids may be a measure of their relative conductivities; but the solution-pressure ratio $\mathrm{N}_1/\mathrm{N}_2$ for the metals seems to be exponentially connected with their chemical activity, *e. g.* their heat of oxidation.

It is needless to point out that in the above equation most voltaic cells are included, at least if one is content to omit from consideration the inert non-migrational non-chemical junction of the two metals.

Some remarkable cells of this kind have been suggested, where the liquids overpower the metals, so to speak; none more so than a cell specified by Hittorf *, who says that by surrounding copper with a solution of a cyanide it can be made electropositive to zinc, so that copper shall go into solution and zinc shall be turned out, being deposited upon a zinc plate.

The scheme for this cell of Hittorf's is said to be

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{K_2SO_4} \mid \mathrm{KCN} \mid \mathrm{Cu}.$$

The object of the K_2SO_4 is, as in many of these cells, to interpose a neutral harmless substance between two solutions which otherwise would precipitate each other.

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* *Zeits. f. physical. Chem.* 1892, vol. x. p. 592.

Perhaps some one will set up a cell of this kind and verify the statement; though Hittorf's is very high authority.

Chapter VI.

Electron or Corpuscular View of Voltaic Action.

The theory which seeks to reduce the whole material universe to electric charges, their motions and interactions, constitutes a gigantic subject upon which it is scarcely rash to predict that a great deal will be said during the ensuing century.

Dr. Larmor (Phil. Trans.) seeks not only to explain physical phenomena in general by means of electrons, but also to explain the electron itself as an intrinsic æther strain. Prof. J. J. Thomson (Phil. Mag. *passim*, especially December 1899) adduces experimental facts in favour of the real and even isolated existence of such charged corpuscles, whether they be pure electrons or not.

Meanwhile the mode of expression in term of corpuscles is less ambitious than that in terms of electrons, though both are revolutionary and striking enough. Let us take it then as granted hypothetically that every material atom is built up of the same fundamental corpuscles, each with the usual ionic charge; a hydrogen atom being composed of about 500 of such corpuscles of opposite signs, a sodium atom of about 10,000, and a mercury atom of about 100,000 of them.

Let every electric current (except a displacement current in free space) be associated with a transfer of corpuscles, a convection of ionic charges, whether in liquids or in metals or in gases; the only difference being that in liquids the travelling corpuscle carries the whole atom with it, whereas in gases it can travel in some cases isolated from all the rest of an atom*, though in other cases it may be clogged with a considerable molecular aggregate of atoms†; while in solids presumably a corpuscle can only travel by being handed on from one atom to the next: though a shift inside each atom will correspond to a polarisation current.

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* J. J. Thomson, Phil. Mag. Dec. 1899.

† *Cf.* Chattock, Phil. Mag. Nov. 1899; also Rutherford, Townsend, Wilson, &c., Phil. Trans.

At an electrode the corpuscle leaves its ion to do the best it can, and passes on into the metal, each atom receiving it into its atomic grouping and instantaneously passing on an equal corpuscle to the next: or at least that is what I suppose to happen, consistently with the hypothesis. At a junction of two metals, then, a corpuscle which had formed part of an atom of one metal finds itself received and incorporated by a different kind of atom. This may clearly involve a gain or a loss of energy, and accordingly some propelling or opposing E.M.F. It may be expressed if we choose somewhat in the language of Helmholtz's hypothesis, that one metal attracts electricity more forcibly than another. If the excess energy takes the form of molecular agitation, such a procedure may entirely account for the Peltier and Seebeck phenomena.

I have spoken of it above (p. 383) as a futile kind of "transmutation": "transmutation" because a portion of the substance of say an iron atom enters into and becomes part of the substance of a copper atom: "futile" because there is no effective conversion of iron into copper, since the amount of each metal remains the same as before.

If corpuscles could be passed into a metal without being passed out again, there would be a kind of transmutation, and this is hypothetically done when a body is charged with negative electricity; it has gained corpuscles which do not belong to it. But the fact that they do not belong to it—being evidently there on sufferance and tending to escape as soon as possible—shows that there is no real transmutation: a charged sodium atom is not a mere sodium atom but a sodium monad ion; it has one negative corpuscle too many.

It might be thought that by giving to a metal charges of positive and negative electricity alternately some extra atoms could be built up: but unfortunately this is not consistent with the fact that, under known circumstances, the negatively charged corpuscle is the mobile ingredient; so that superposing a positive charge on a negatively charged atom is not adding something to the corpuscles already there, but is removing the extra negative corpuscle and another as well; taking the atom down therefore instead of building it up, and leaving a void which automatically fills itself up whenever it gets a chance. It is just possible that some kind of effective transmutation might be effected in an electric spark or arc with different materials on either side of it; like a substance passing over from one crystalline form to another.

Whether combination of atoms takes place across any junction when a current passes, appears to be merely a question of relative mobility of corpuscles and atoms. If the atoms are free to move, if it is easier to move an atom across the interface than to detach from it a corpuscle, then combination occurs, and the conduction is then necessarily on one side essentially electrolytic; and at a liquid-liquid junction there may be double atomic freedom and complete electrolysis. But if the corpuscles are more detachable than the atoms, then the conduction is metallic and no alloy is formed.

But now, pressing further the osmotic pressure view, if the metals can evaporate into a liquid they ought perhaps to be able to evaporate into each other, and so the E.M.F. at a junction ought to be calculable as

$$E = R\epsilon T\left(\qquad\right)\log\frac{n}{n'},$$

where the $\frac{n}{n'}$ may be taken as the ratio of the metallic densities; but what shall we put into the brackets for the ionic velocities? Not ionic velocities at all, but corpuscular velocities, and these corpuscular velocities may differ by reason of the different viscosity or obstruction offered by each metal; which again perhaps may be proportional to the density; but the solution can hardly be treated as a weak one, or the gaseous laws as applicable.

If gaseous laws are applicable to the corpuscles inside metal, the value of their characteristic constant R will be 500 or 600 times the value for hydrogen; but inasmuch as their m, or ϵ their electrochemical equivalent, is 1/500 or 1/600 of the hydrogen value, the resulting $R\epsilon T$ comes out just as usual.

The viscosity or obstruction offered by metal is probably its electrical resistance; and so the corpuscular velocity in each may be proportional to the conductivity.

Conductivity in a liquid means greater mobility of the ions, conductivity in a metal may mean greater mobility of the corpuscles; hence perhaps the E.M.F. of a metallic junction might be something like this:

$$E = \cdot 114 \frac{k-k'}{k+k'} \log \frac{m/\rho}{m'/\rho'} \text{ volt},$$

where the k are conductivities and the m atomic weights and the ρ densities.

I would suggest that the curious deterioration suffered by some thermo-electric piles with lapse of time, especially those used for generating a fair amount of power, has never so far as I know attracted much attention or been thoroughly investigated. It may be merely mechanical, due to alternate heating and cooling, but it may possibly be due to something of greater interest.

The corpuscles clinging to atoms are rather like ions clinging to solvent; so perhaps in a metal the negative corpuscles move with velocity

$$u = u_1 \left(\frac{1}{Ne} \frac{dp}{dx} + \frac{dV}{dx} \right)$$

where the intrinsic velocity u_1 is large; while the positive corpuscles move with velocity

$$v = v_1 \left(\frac{1}{Ne} \frac{dp}{dx} - \frac{dV}{dx} \right),$$

their intrinsic velocity v_1 being very small.

But in a homogeneous metal itself these speeds u and v are perhaps equal; indeed where there is no potential gradient or driven current they must be equal.

Are they equal at a metallic junction too ?, or is anything kinetic occurring there at all?

There must be a stress or polarisation or double layer or something statical at such a junction; and a statical condition can be simulated by kinetic equilibrium. What are the arguments?

When a zinc surface is illuminated with ultra-violet light J. J. Thomson found that it does not throw off corpuscles unless it is negatively electrified. The ultra-violet light may be said to detach them, but it takes electrification to throw them off.

So at a junction of two metals when no current is being passed it may be that there is no interchange of substance; but the interchange may or must begin as soon as a current flows; and if the A aggregation has more potential energy then the B aggregation there will be a force urging the corpuscles to flow from A to B.

In a gas the negative corpuscles are by far the most mobile; indeed the positive corpuscles seem unable to move except with their atoms electrolytically. It may be that even inside a metal the negative corpuscles are likewise by far the most mobile, being readily handed on from one atom to the next, this process constituting metallic conduction; while the positive corpuscles remain attached to their atoms, which except in an electrolyte or a substance with some electrolytic properties are not subject to locomotion at all. Assuming this mobility of corpuscles of one sign solely, they are urged along a gradient of temperature in a metal for two reasons: one a mechanical force equivalent to a dp/dx acting on an element of volume, or $1/n$ of this per corpuscle; the other an electrical force dV/dx acting on its electric charge e.

When there is no current these forces must balance. So

$$\frac{1}{n}\frac{dp}{dx} - e\frac{dV}{dx} = 0,$$

or

$$dp = ne\,dV.$$

Now proceeding as usual without compunction to utilise the gas-analogy

$$p = nmRT,$$

we have

$$ne\,dV = mR\,d(nT)$$

or

$$dV = m/e\,.\,RT\,d\log(nT).$$

This is the E.M.F. that acts along the gradient of temperature, giving rise to a reversible evolution of heat and representing the coefficient of the Thomson effect, σ, called the specific heat of electricity in a metal, such that the work done in transferring a charge q up a difference of temperature dT is $qdV = q\sigma dT$, or

$$\sigma = \frac{m}{e} RT \frac{d}{dT} \log (nT).$$

Hence for a circuit of two metals a and b

$$\sigma_a - \sigma_b = R\epsilon T \frac{d}{dT} \log \frac{n_a}{n_b}.$$

And by ordinary thermodynamics this is related to the Peltier effect at the junction and to the resultant E.M.F. in the circuit by the equations

$$\int \frac{\sigma_a - \sigma_b}{T} dT = \frac{dE}{dT} = \frac{\Pi}{T};$$

therefore

$$\Pi = R\epsilon T \log \frac{n_a}{n_b}.$$

Now n represents the number of active corpuscles in unit volume, and this number is a function of the temperature; and its rate of change probably depends on the number already there and on a coefficient characteristic of the metal; $\frac{dn}{n} = \alpha\, dT$, say; therefore let $n_a = ae^{\alpha T}$, $n_b = be^{\beta T}$.

In substances whose conductivity increases with temperature α will be positive, but in metals it is usually negative, and at absolute zero the conductivity would rise to a maximum value corresponding to the maximum corpuscular concentration a or b.

So
$$\Pi = R\epsilon T \log \frac{a}{b} + (\alpha - \beta) R\epsilon T^2;$$

whence the neutral point is

$$T_0 = \frac{\log b - \log a}{\alpha - \beta},$$

and

$$\sigma_a = \alpha R\epsilon T = k_a T,$$

and

$$\Theta_a = \tfrac{1}{2}\alpha R\epsilon(T_1^2 - T_2^2),$$

and

$$E = (\alpha - \beta)R\epsilon(T_1 - T_2)(T_0 - \tfrac{1}{2}(T_1 + T_2)),$$

or

$$P_a = \alpha R\epsilon(T_0 - \overline{T}).$$

So that our hypothesis does fairly well to express thermoelectric facts; but, unless the opposite sign of corpuscles is attended to, it does not account for the fact that the coefficient σ is positive in some metals and negative in others; though it suggests an opposite sign for σ in metals and electrolytes, because α changes sign along with the temperature-coefficient of conductivity.

To divide metals into two classes we must not suppose that the negative corpuscles do all the travelling: if they did, moreover, the Hall effect, the magnetic influence on the current, corresponding to the magnetic curvature of cathode rays, would be much greater than it is. The facts that the Hall effect is small, and that it has different signs in different metals, suggest, as J. Larmor points out, that the speed of the negative and positive corpuscles or electrons is nearly equal, but that in some metals the positive travel slightly faster, in other metals the negative: the difference being subordinate and secondary.

It will turn out on this view that the "specific heat of electricity" σ, the coefficient of the Thomson effect, has the same sign as the coefficient of magnetic curvature of current, the Hall effect. For proceed with our theory of metallic conduction treated as a convection of charged corpuscles of both kinds, with u/v the Hittorfian migration ratio of negative to positive corpuscular velocity, under the action of unit force; and write down as in electrolysis that the resultant motion must be equal in opposite directions,

$$u\left(\frac{1}{n}\frac{dp}{dx} + e\frac{dV}{dx}\right) = v\left(\frac{1}{n}\frac{dp}{dx} - e\frac{dV}{dx}\right),$$

or

$$\frac{dV}{dp} = \frac{1}{ne}\frac{u-v}{u+v},$$

or

$$dp = ne\frac{u+v}{u-v}dV.$$

Then the various thermoelectric quantities get written exactly as above, except that the new factor $\frac{u-v}{u+v}$ must be everywhere introduced.

It is worth noticing that

$$ne(u+v) = \frac{C/A}{dV/dx} = \frac{\text{current-density}}{\text{potential-gradient}} = \text{specific conductivity} = \frac{1}{\rho};$$

wherefore

$$\sigma = \frac{dV}{dT} = \rho(u-v)\frac{dp}{dT}$$

$$= \rho m R(u-v)\frac{d}{dT}(nT).$$

This form is instructive as showing that, other things being equal, highly resisting substances are likely to form the best thermoelectric materials. The metals of high conductivity have, in fact, feeble thermoelectric power; metals like bismuth and antimony are poor conductors; and the contact force between insulators, or still better between an insulator and a conductor, may be enormous.

But for most purposes the previous form of expression is handier, so introducing the migration ratio $r = u/v$ we get

$$\sigma = R\epsilon T\frac{1-r}{1+r}\frac{d\log(nT)}{dT};$$

and so on for Π and E as before when two metals are employed, only with the new relative migration factor which permits ready change of sign; and it must be remembered that the corpuscular migration ratio r, as well as the corpuscular detachment number n, may differ in the two metals.

CHAPTER VII.

Helmholtz's View of Electric Mass-Affinity.

The doctrine that matter has a specific attraction for electricity * leads to many of the same conclusions as the supposition that positive or negative electricity inside a substance has a real specific heat, and the two modes of statement may be considered together; but we may speak in the language of Helmholtz's hypothesis, as being the more important of the two, indeed the only one seriously upheld as a physical reality. As has been suggested above, p. 389, it is to some extent ambiguous, however; for it is not certain whether the affinity or attraction is effective at a metal-æther free surface or at a metal-metal junction. As usually stated, the attraction is supposed to be an affair of mass or bulk and not of surface, though no doubt any such internal volume electric stress would give rise to something analogous to electrical surface-tension †; but the whole may be really and essentially superficial, having to do with the free surface only; and in that case it is difficult to distinguish it from chemical affinity, unless it can truly be shown to be independent of the presence and nature of surrounding adjacent matter. Even so it may be considered as an early and crude statement of certain consequences of the electron theory of matter, rather than as a distinct and independent theory (*cf.* J. Larmor, Phil. Trans. 1897, vol. cxc. p. 271).

However it be regarded, it is plain that the effect of an attraction between matter and electricity must display itself at a transition or boundary layer, and although it has been customary to concentrate attention on the metallic (*e.g.* the copper-zinc) junction in this connexion, it is by no means probable that that is so efficient or complete a transition as is the free air or æther surface of either metal; nevertheless these surface actions have secured too little attention.

The proofs that have been given, for instance, of the value of the Peltier effect, and its connexion with contact force, or boundary force as we might now call it, are accustomed more or less completely to ignore the air boundaries; employing an open circuit with the object of avoiding obvious neutralising or compensating forces at other junctions, but forgetting that opening a circuit necessarily introduces one *more* boundary, not one *less.*

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* For references see Phil. Mag. October 1885, p. 377.

† Just as Laplace's K gives rise to capillarity.

Dr. Larmor has been good enough to tell me of a "proof" in Parker's 'Thermodynamics' (1894 edition) that on Helmholtz's view the Peltier coefficient at a metallic junction is proportional to the rate of change of the junction force there with temperature; a proof somewhat on the same lines as that given independently by Lord Kelvin in the Proc. Roy. Soc. Edin. vol. xxii. page 118, Session 1897–8; but neither proof in reality establishes anything specially limited to the metallic junction; the whole of the junctions are really laid under contribution, a fact which is half recognised by Lord Kelvin, though not by Mr. Parker.

In order to save other people from working through these proofs I may reword them in a simpler and briefer fashion, using language appropriate to the mass-affinity doctrine, but incidentally throwing in the symbol σ so as to include also the essence of the specific heat idea.

Let a charge of electricity given to a metal be held there by an intrinsic attraction or mass-affinity; it will have a special affinity-energy in addition to the energy of its ordinary electrical interactions with other charges: call this surplus energy, at the absolute temperature θ,

$$u=u_0+\int\sigma d\theta.$$

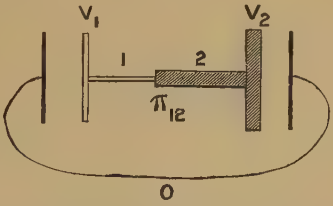
The corresponding entropy is

$$s=s_0+\int\frac{\sigma d\theta}{\theta}=s_0+\int\frac{du}{\theta},$$

so that

$$du=\sigma d\theta=\theta ds.$$

Consider an open circuit of two active metals and one neutral substance, *e.g.* Zn, Cu, and Pt, or 1, 2, and 0, with air-gaps forming condensers as in the diagram ; the condensers being charged to the potentials V_1 and V_2 respectively by the differential electric affinities at work.



Now transfer unit charge reversibly from one condenser to the other, *i.e.* from potential V_1 to V_2, by shifting the neutral plates ; the work done, equivalent to loss of energy, has usually been written as

$$V_2 - V_1 = \Pi_{12} + u_1 - u_2,$$

but it ought to be written

$$V_2 - V_1 = \Pi_{01} + u_1 + \Pi_{12} - u_2 + \Pi_{20}.$$

The total entropy change is zero,

$$\frac{\Sigma\Pi}{\theta} + s_1 - s_2 = 0,$$

or, writing Π for $\Sigma(\Pi)$,

$$\Pi = \theta(s_2 - s_1),$$

wherefore

$$V_2 - V_1 = u_1 - u_2 - \theta(s_1 - s_2),$$

or

$$V + u - \theta s = \text{constant}.$$

But

$$u - u_0 = \int \theta ds = \theta s - \int s d\theta,$$

so

$$V - \int s d\theta = \text{constant},$$

or

$$\frac{dV}{d\theta} = s,$$

or

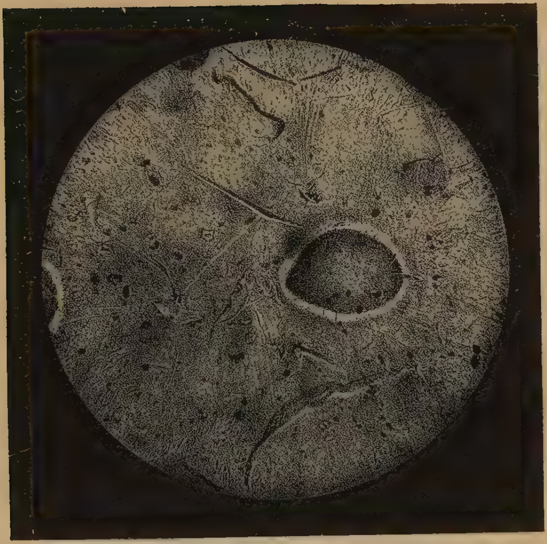
$$\frac{\Pi}{\theta} = s_2 - s_1 = \frac{d}{d\theta}(V_2 - V_1) ;$$

the result to be proved.

But there is nothing here more than has been admitted in this paper over and over again.

If surface boundary forces are supposed zero, if electricity can enter or leave the free surface of a metal without aid or obstruction, then $V_1 - V_2$ must represent the only remaining force, viz. that at the metallic junction; and the only Π will be situated there; but if there are other boundary forces, then $V_1 - V_2$ represents the whole E.M.F. of the circuit, and not the localised junction force at all, and Π_{12} is not necessarily the sole Peltier effect. The metallic junction force may still be measured by Π_{12}; the combined entropy of the boundary forces is $\Sigma\Pi/\theta$; and this entropy is proved equal to $dE/d\theta$, a remarkable and interesting but long known fact.

Returning to the theory of Helmholtz, which was stated first so long ago as 1847, and elaborated to some extent in his brilliant "Faraday lecture" of 1881, it is undoubtedly very important; it may be regarded as the precursor of, and therefore to some extent superseded by, the electron or corpuscular theory of matter: a theory which represents the natural outcome, in the light of recent experiments, of that "atomic" view of electricity which, started by Clerk Maxwell in an inspired phrase, adopted and expanded by Dr. Johnstone Stoney and others, is now in the preceding pages attempted to be applied, in conjunction with ideas derived from the treatment of osmotic pressure by physical chemists, to an explanation of thermoelectric action on the gaseous analogy.



R. Mintern lith.

Mintern Bros. imp.

XXVIII. *An Electric Micrometer.* *By* Philip E. Shaw, *B.A., B.Sc., Lecturer in University College, Nottingham* *.

30

Preliminary.

In the summer of 1897, I was engaged in investigating some of the conditions which conduce to high efficiency and stability in a telephone system.

The ultimate product of the system is, of course, vibration of the receiver-diaphragm; so that, *ceteris paribus*, any change in the apparatus, or connexions, which produces increased amplitude of that diaphragm, makes for efficiency.

Suppose now, for instance, that the winding of the receiver-electromagnet is altered, then, passing in constant sound to the transmitter, if we measure the movement of the receiver-diaphragm before and after any such change, we shall be able to judge of the efficacy of the change.

Such was the idea that led to the making of the measuring arrangement to be described, which has proved to be suitable both in delicacy and adaptability for diaphragm movements.

I. Experimental Methods.

1. *Apparatus.*

First Form.—The principle employed is to measure the exact place of contact of two surfaces which, on meeting, complete a circuit containing a telephone. A special spherometer was made with great care; the disk was 8 cm. in diameter, graduated into 500 parts, the screw-pitch was $\frac{1}{2}$ mm.; the graduations were subsequently corrected against dead-hard pieces of steel 5, 10, 15, &c. mm. long, verified by the Standards Department of the Board of Trade, the errors being very small.

The three outer legs of the spherometer were removed and the frame (AB) of the spherometer was fastened firmly to the thick board (XX) (fig. 1), then the end of the screw (S) abutted against the long arm (CL) of a lever which was held against it by a spring, while the short arm (CM) carried a small brass rod holding in its end a platinum wire beaded at the end (*a*).

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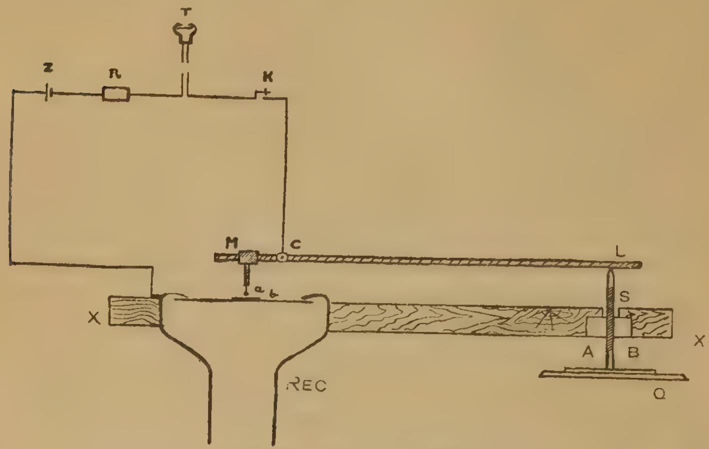
* Read March 23, 1900.

Fig. 1.



The telephone-receiver (*Rec*) is firmly fastened in the board (XX) so that the centre of the diaphragm, which carries a small platinum plate, is opposite to the platinum bead. Then the circuit, consisting of the cell (Z), the resistances (R), the observing-telephone (T), the key (K), and the contacts, is completed when (*a*) and (*b*) meet, which can be brought about by a forward or backward movement of the screw (S).

As seen in the figure, the graduated disk (G) has a pulley on the back of it; a cord passes round this and a series of other pulleys, so that the screw can be worked to and fro by the observer without touching the screw directly by hand. By the use of the pulley-string, vibrations are not so readily transmitted from the hand, and, moreover, by that means the observer can work from a convenient distance, reading the disk (G) by a telescope.

The telephone (T) has long flexible wires, so that the observer can have it attached to his head and hear the contact made, while at the same time he is watching the disk (G) for its position. In this manner the position of the "break" of contact (*a*) and (*b*) can be observed.

Suppose now a steady current passes in the receiver (*Rec*), the diaphragm will move to a new position and remain there; then the observer can quite easily follow, and measure, its movement.

The wooden frame carrying the apparatus was heavily weighted with lead and supported on soft rubber balls, to insulate it against vibrations.

The ratio of the lever-arms was about 10 : 1. By using a telescope, each graduation on the disk (G) could be divided by eye into ten parts; each of these corresponded to a movement of the screw-end of $\frac{1}{5000}$ of $\frac{1}{2}$ mm., or 10^{-5} cm., or at the other end of the lever to 10^{-6} cm. about.

Second Form *.—In the next attempt (fig. 2, p. 438), the single brass lever was replaced by three levers of aluminium, working in co-operation, so that the joint leverage ratio could be made 1000 : 1.

The levers are made of aluminium bar ($\frac{1}{4}$ in. × $\frac{1}{2}$ in. section) about 15 inches long; the pivots are of steel, their ends being pointed to rather acute cones. The lower bearings for the lever-pivots are provided in brass plates let into brackets, whilst the upper bearings are turned in the screw-ends. The brackets which carry these top bearings are made of stout brass bar, bent twice at right angles and firmly screwed to the frame and to the wooden brackets.

The screws mentioned before have lock-nuts bearing on the brass brackets so that the pivots can be tightened up in their bearings as required. Each lever is balanced by a lead weight screwed to its short arm, the object being to have the centre of gravity of each lever over the lower bearing so as to have no side pressure and consequent wearing of the upper and lower bearings. The lever-ends are kept firmly in contact with their bearings by the action of the helical brass springs attached to the levers and to the frame; these springs are fairly strong, so as to render the pressure throughout the lever-system firm and reliable in all positions.

This point is of obvious importance, for any backlash in the screw or looseness of the pivots in their bearings, would be nullified by the action of the springs; so that we should still have firmness in the lever-system.

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* Exhibited at the Royal Society Conversazione on May 8, 1900.

The bearings by which the ends of the second lever press on the other two are moveable, so that we can obtain different leverages by clamping them in different positions. The greatest leverage thus obtainable was about 1000 : 1, and the least about 100 : 1. A centimetre-scale was marked on the levers, so that the clamps could be brought to any desired position as often as required.

The arrangement for holding the telephone-receiver, on which the experiments are made, will be described next.

There is a massive hollow cylinder of wrought iron 15 cm. long, 9 cm. diameter, the metal being about $\frac{1}{2}$ cm. thick. The telephone-receiver is screwed to a ring on the further side of the cylinder, so that, on looking from the back, the whole diaphragm may be seen. There is also a screw cut on the outside of the cylinder, which works in a screw cut in a ring of iron, imbedded in, and screwed to, the wooden frame.

A lock-nut is provided so that when the cylinder has been screwed into position it may be tightened and held rigid.

By having such a massive and well-fitting support for the receiver, firmness and ready adjustability are secured for it.

Having briefly described the essential parts of the apparatus, we now proceed to consider the various adjuncts separately.

2. *Supports.*

The table is supported from the foundation of the building by brick piers. Vibrations passing through to the table would be mostly of high frequency, and so should not be transmitted by a succession of heavy masses separated by springs and layers of indiarubber. The series was as follows:

(1) Blocks of solid pure rubber on the table; (2) a lead slab of 180 lb.; (3) four soft rubber balls; (4) a board weighted to 50 lb.; (5) four soft rubber balls; (6) the large rectangular frame loaded from which hang (7) four rubber springs which hook on to (8) the apparatus, which is loaded to about 50 lb.

The above provisions against tremors were sufficient for the most delicate work, provided that no violent vibrations were started in the neighbourhood. The motion of carts in the streets, violent wind-gusts, or the working of near factory-machinery were fatal.

An attempt was made to find roughly the efficiency of the various layers in the series, as follows. I found the vibration amplitude in the apparatus (1) when all the layers were in, (2) when the upper one was removed, (3) when two were removed, and so on. By actual measurement the amplitudes were found to be roughly (using $\mu\mu$ as unit):—

$$1, \quad 10, \quad 15, \quad 40, \quad 100;$$

i. e., (1) when the apparatus was suspended from the door-springs the amplitude was $1\mu\mu$; (2) when the apparatus was unhooked from the springs and rested on the other layers, we had $10\mu\mu$, and so on.

The above measurements show that solid rubber is more useful than the hollow rubber balls (whose elasticity depends greatly on compressed air), and also that little advantage is obtained by the second layer of balls.

3. *Covers.*

Temperature-changes in the levers, and contacts, may arise in many ways, but especially from draughts of air and radiation.

To provide against these, and also against moving dust in the air, different wooden covers were placed over (1) the contacts, (2) the levers, (3) the telephone-receiver and its enclosing metal cylinder. After some trial these precautions were found inadequate ; so the whole apparatus was wrapped in thick felt. This covering served well, not only in maintaining a constant temperature but also in damping sound-vibrations, which in some cases, before its application, produced a chattering of the contact of about the frequency of the sounds themselves. By taking such extensive precautions, immunity from these disturbances was obtained, even in the extreme case when very many gas-jets were burning in the room.

As regards dust, it was anticipated that great trouble would arise, for even small particles suspended in the air would be large compared to the smallest distances to be measured by the apparatus: such particles would seem likely to remain suspended in the air about the contacts, even after the covers had been put on and the air had remained calm for a long time. Also we might suppose that the contacts, being electrically charged, would be centres of dust collection, so that in fact we should have a clogging of the contacts from dust, just where it was desirable that they should be specially clean.

To avoid these baneful effects, a special atmosphere round the contacts was provided; air was driven at a uniform rate through sulphuric-acid bottles, then through cleaned cotton-wool, then through a helical tube in a water-bath, then into the compartment containing the contacts. It was hoped that the contacts would thus have round them dry and dust-free air of uniform temperature. But this plan was soon abandoned, for this special air was found to produce comparatively rapid and great temperature-fluctuations at the contacts; so that the air-temperature was much more steady before than after the "remedy" was applied.

The best plan, therefore, seems to be to give the chamber containing the contacts time to settle to its own state of temperature-equilibrium after the covers are on.

What part, if any, dust really plays, the author has not ascertained, for in all the later work it has been left out of account.

4. *Contacts.*

Platinum was first used for both contacts; but as there seemed to be a slight permanent yielding of the surfaces even under the very small pressures used, iridio-platinum (20°/₀ iridium) was substituted for it and used generally afterwards. The iridio-platinum plate (4 mm. square) used was soldered to the surface of the iron diaphragm of the receiver, care being taken to use a small soldering-iron so as to avoid great heating and consequent buckling of the diaphragm.

It was found requisite to clean the contacts thoroughly and often, so as to keep them in good working order. When the two surfaces are quite right, the sound heard at "make" and "break" is sharp, and has a clear ring; but when not in good order a dull or "wheezy" sound is heard, which may in some cases continue over a distance of as much as 10^{-5} cm.; evidently in such a case the contact is only partial over this distance.

On consideration, it will be seen that this disorder may be due to dust or oxide or other impurity on the surfaces; but conceivably it might be attributed to a gradual grazing contact made between two projecting parts of the surfaces, so that contact is not complete till the contacts are pressing one another appreciably.

Whatever the cause, this state of the contact must be removed. In some cases it suffices (1) to press together and release the surfaces several times in succession; (2) to make and break current several times when the surfaces are in contact; (3) to rub the surfaces (*in situ*) with some clean tape. But it often happens that all such ready means fail: then the contacts must be dismounted, polished, and cleaned as follows:—

Place each contact in turn in the lathe, (1) rub with the the finest emery-paper, (2) polish with rough paste, (3) polish with fine paste, (4) rub with caustic potash and wash, (5) rub with hydrochloric acid and wash and dry, (6) rub well with clean tape. A clean surface having very small roughnesses should be the result of this process.

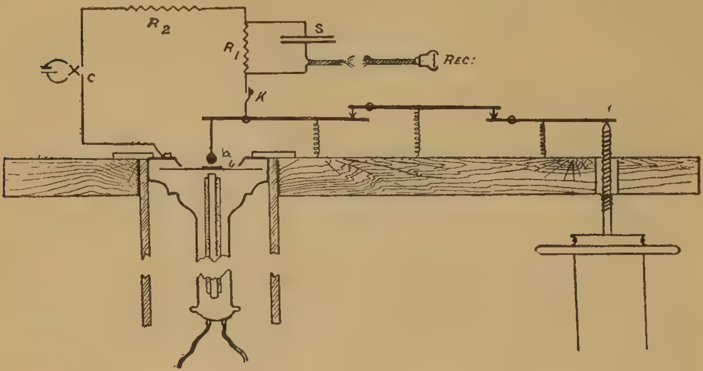
It would seem desirable to produce the highest possible polish, for doubtless the irregularities on the surfaces, even under the best conditions, are large compared with the smallest measurements to be made. The ideal surfaces would be a geometrical sphere and geometrical plane, whereas the actual contacts would, if very closely examined, appear in point of roughness more like mountainous regions.

5. *Circuits.*

The simple circuit, shown in plan in fig. 1, was superseded by one shown (also in plan) in fig. 2, where we see the observing-receiver (*Rec*) and a condenser (S) put together as a shunt to the large resistance (R_1). Another, small, resistance (R_2) is used, and the cell (C) can be reversed.

If the circuit is completed by the touching of the contacts (*a*, *b*), there is (1) a momentary rush of electricity to charge the condenser, (2) a steady current of small amount through the resistances R_1 and R_2. (1) soon ceases. On "breaking" circuit, by the separation of *a* and *b*, the condenser will be discharged through R_1, and so, at the next "make," will receive a new charge, and so on.

Fig. 2.



Thus at both "make" and "break" a rush occurs through the telephone (*Rec*), giving the observer evidence of them; the rush lasts for a very short time, but it can be made powerful enough to serve our purpose.

By the use of a condenser we obtain a large impulsive flow just when required, *i. e.* at "make" and "break;" hence the contact is not disturbed by a steady flow (and consequent heating &c.) during the interval between make and break.

A simple example will show the value of this method. Consider two cases:—

(1) $S = 0{\cdot}1$ microfarad.
$R_1 = 10{,}000{,}000\ \omega$.
$R_2 = 1000\ \omega$.
E.M.F. $= 1{\cdot}0$ v.

Then, neglecting the small steady current, the quantity passing impulsively at make is

$$Q = 0{\cdot}1 \times 10^{-6} \times 1{\cdot}0 = 10^{-7} \text{ coulomb.}$$

(2) Suppose we used a simple circuit as in fig. 1:—

$R = 100{,}000\ \omega$ (this is the most attained in practice).

E.M.F. $= 1{\cdot}0$ v.

Then the quantity passing during 1 second after make would be:—

$$Q = 10^{-5} \times 1{\cdot}0 = 10^{-5} \text{ coulomb.}$$

This is 100 times as large as for case (1); and if the surfaces were in contact for more than 1 second, the ratio would be even larger.

The plan in working is to reduce S and increase R_1 and R_2 down to the limit of comfortable sounding of the receiver. By this care the surfaces can be used continuously for 2 to 8 hours, whilst when not in use they seem to remain unchanged.

Suppose that by the passage of electricity at the contact the platinum wire rose in temperature $\frac{1}{100}$ of one degree, it would if 1 cm. long expand about 10^{-7} cm., *i. e.* one of our smallest measurements. Hence it is that large currents are to be deprecated.

6. *Setting the Contacts.*

Suppose the apparatus set up, and the contacts clean, and that we wish to get the contact position ready for taking measurements. The observer arranges the observing telephone (which is provided with long flexible wires) on his head, puts on the cells used, and goes to the left-hand of the apparatus (fig. 2). He then screws up the iron cylinder with its receiver till contact is heard, then he tightens the lock-nut till, on gently tapping, the contact is heard to rattle; then he is sure that the surfaces are approximately near one another and, probably, not touching. Then he puts on the cylinder cover and all other covers, and takes a seat at the right-hand end of the apparatus, where, by the motion of the pulley, he can obtain the exact contact position, and observe the graduated disk with the telescope.

In the earlier observations, when the distance was required between any two positions, they were both read and entered (say for instance $48{\cdot}92 \sim 49{\cdot}43$, diff. $= 0{\cdot}51$), but subsequently readings were entered always as differences; this method was less tedious and conducive probably to greater accuracy.

II. Observations and Results.

Passing now to the experimental results, we have them arranged as follows :—

(1) Preliminary.
(2) Calibration of the instrument.
(3) Measurement of the diaphragm movement throughout the range of sound impulses, from the smallest audible ones to such as are very loud.
(4) The damping of the diaphragm.

(1) *Preliminary.*

It was necessary at the outset to ascertain whether this contact method was delicate and consistent, and if so under what conditions. Several months were occupied in endeavours to obtain consistent readings of the contact position of the diaphragm ; detail after detail was improved in the apparatus as its requirements were discovered. Three tables will be given as samples of the readings taken.

Table I. explains itself.

Table II. shows how the displacement of the diaphragm due to a steady current is taken. Column 2 gives the diaphragm position before, and column 4 after current is put on. Column 3 is found by assuming the creep in contact uniform. Column 7 shows the movement in terms of the unit $\mu\mu$ (10^{-7} centim.). This table was obtained in earlier work, and it is not specially accurate, but it serves to show that the readings are very fairly consistent.

Table III. Here a measurement was made of the throw of the diaphragm ; the electromotive force and resistance used are known, but, on account of self-induction in the receiver, the current does not rise at once to its full amount. It is this uncertainty about the action of self-induction which has precluded the use of the throw in subsequent work.

TABLE I.

Consecutive Readings showing the constancy of the contact-position under favourable conditions, and also to prove the small difference that exists between "make" and "break" under certain conditions. The last column gives the difference, if any, roughly in terms of the unit 10^{-7} cm.

That the readings are so very steady as a whole is due in great measure to the fact that they were taken in the late afternoon, when the temperature in the room was nearly stationary.

July 30th. Time.	Make.	Break.	Difference.	10^{-7} cm.	July 30th. Time.	Make.	Break.	Difference.	10^{-7} cm.
5.34	40·6	40·7	0·1	(10)	6.4	40·7	40·6		
5	40·9	40·9			5	40·6	40·7		
6	40·9	41·0	0·1	(5)	6	40·65	40·8	0·15	(15·5)
7	40·85	40·9	0·05	(10)	7	40·6	40·7	0·1	(10)
8	40·7	40·7			8	......	......	Interruption.	
9	40·7	40·7			9	......	......		
40	40·8	40·8			10	......	......		
1	40·5	40·6	0·1	(10)	1	......	......		
2	40·9	41·0	0·1	(10)	2	......	......		
3	41·0	41·0			3	......	......		
4	40·7	40·9	0	(21)	4	......	......		
5	41·1	41·1			5	40·6	40·7	0·1	(10)
6	40·95	40·95			6	40·8	40·8		
7	41·0	41·0			7	40·6	40·7	0·1	(10)
8	40·8	40·8			8	40·7	40·7		
9	40·8	40·8			9	40·65	40·75	0·1	(10)
50	40·8	40·8			20	40·7	40·7		
1	40·9	40·9			1	40·8	40·8		
2	40·9	40·9			2	40·9	40·9		
3	40·9	40·9			3	40·8	40·8		
4	40·7	40·7			4	40·5	40·5		
5	......	......	Interruption.		5	40·3	40·3		
6	......	......			6	40·5	40·5		
7	40·7	40·7			7	40·7	40·7		
8	40·7	40·7			8	40·55	40·55		
9	40·7	40·7			9	44·55	40·55		
6.0	40·8	40·8			30	40·6	40·65	0·05	(5)
1	40·7	40·7			1	......	......	Interruption.	
2	40·7	40·7			2	40·9	41·1	0·2	(21)
3	40·8	40·8			3	40·8	40·8		

Thus during the whole of one hour the highest reading was 41·1, and the lowest 40·3, the difference being only 8×10^{-6} cm.

Table II.

Consecutive Readings showing that the Diaphragm may be relied on to give uniform readings, when subject to repeated displacement and return. The steady creep in readings seen in column 2 is due to fall in temperature.

Aug. 12th. Time.	Normal Contact.		Displacement Contact.	Movement.	Mean.		Current &c.
	Observed	Assumed.			Actual.	10^{-7} cm.	
6.12	2·10						1,430 V. 10,000 ω.
3	2·00	......	......	......	......	......	
4	......	1·95	1·80	0·15	0·145	15·1	Direct.
5	......	1·87	1·73	0·14			
6	1·80						
7	1·75						
8	......	1·68	1·85	0·17	0·160	16·6	Reversed.
9	......	1·67	1·82	0·15			
20	1·56						
1	1·50						
2	......	1·38	1·20	0·18	0·155	16·1	Direct.
3	......	1·27	1·14	0·13			
4	1·20						
5	1·05						
6	......	0·97	1·14	0·17	0·180	18·7	Reversed.
7	......	0·83	1·12	0·19			
8	0·75						
9	0·62						
30	......	0·60	0·45	0·15	0·155	16·1	Direct.
1	......	0·46	0·30	0·16			
2	0·44						
3	0·30						
4	......	0·27	0·43	0·16	0·180	18·7	Reversed.
5	......	0·15	0·35	0·20			
6	0·10						
7	0·00						

Mean of three direct $=15{\cdot}8\times10^{-7}$ cm.

Mean of three reversed $=18{\cdot}0\times10^{-7}$

TABLE III.

Readings to show the throw of the Diaphragm when a known current is applied. The first four columns are in units of the instrument, the fifth column is in terms of the unit 10^{-7} cm. The current in the sixth column is in terms of a special unit ($1·43 \times 10^{-6}$ amp.).

Normal Contact.	New Contact.	Difference.	Mean.	Corrected Mean, 10^{-7}cm.	Resistance and Current.
23·26	23·29	0·03	0·035	3·6	40,000 ω. C=25
23·45	23·48	0·03			
23·25	23·29	0·04			
23·30	23·34	0·04			
23·85	23·90	0·05	0·045	4·7	30,000 ω. C=33·3
23·76	23·80	0·04			
23·59	23·63	0·04			
23·56	23·61	0·05			
23·40	23·49	0·09	0·072	7·5	20,000 ω. C=50
23·34	23·42	0·08			
23·36	23·42	0·06			
23·70	23·76	0·06			
22·75	22·85	0·10	0·087	9·0	15,000 ω. C=66·6
23·20	23·29	0·09			
23·32	23·40	0·08			
23·31	23·39	0·08			
48·00	48·20	0·20	0·172	17·9	10,000 ω. C=100
47·85	48·00	0·15			
47·78	47·95	0·17			
47·55	47·72	0·17			
46·40	46·82	0·42	0·410	42·6	3,000 ω. C=320
46·25	46·65	0·40			
46·10	46·52	0·42			
45·90	46·52	0·40			
45·40	45·95	0·55	0·58	60·8	2,000 ω. C=470
45·40	46·00	0·60			
45·10	45·67	0·59			
44·97	45·57	0·60			
44·65	45·50	0·85	0·82	85·0	1,500 ω. C=625
44·50	45·30	0·80			
44·05	44·85	0·80			
44·50	45·32	0·82			
42·40	43·40	1·00	1·05	109·0	1,000 ω. C=890
42·35	43·40	1·05			
42·10	43·25	1·10			
41·50	42·50	1·05			

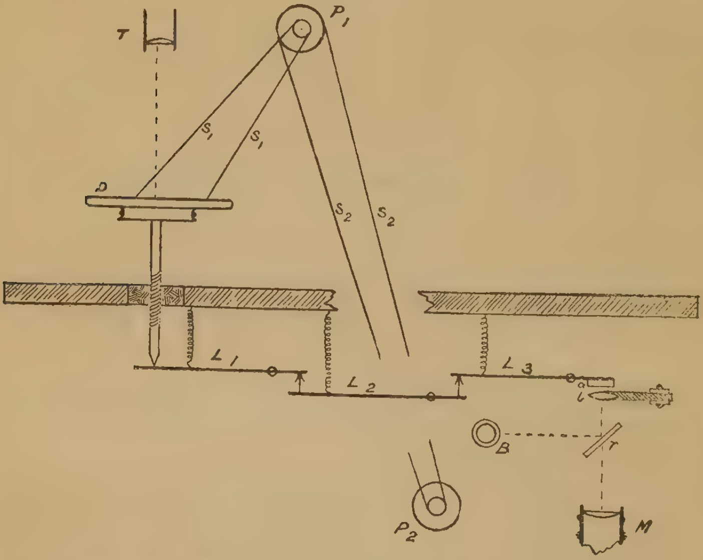
Voltage=1·435 constant.

(2) *Calibration.*

If we assumed that the screw and the divisions of the disk were accurate in all respects, we should still have to determine the joint leverage of the three levers in order to measure any movement; but by the following method of calibrating we can obtain a knowledge of the value of the units on the disk without making even these assumptions.

In fig. 3 is given diagrammatically the plan of the apparatus involved. Fix to the end of the short arm of L_3 a glass plate (a), and close to it a small lens (b) supported from the frame of the apparatus. The plate was a microscope glass slide chosen for its good surface; it was held fast by a screw and nut between the lever and a brass washer.

Fig. 3.



The lens was let into a saw-gate in a brass bar and fixed there by shellac; the brass bar was clamped by screws to a strong upright bar screwed to the wooden frame. Thus the glass plate is fixed to the lever, and the lens is fixed to the wooden frame, both are therefore shielded from the vibrations of the table.

Put up a Bunsen burner B, with sodium light and a glass plate *r* to reflect the rays normally to the glass surface, then an observer at the microscope M will, under favourable conditions, see at the glass surface the centre of a system of Newton's rings. The rings can be made to open out or contract, according as the short arm of L_3 is moved towards or away from the observer. Suppose the rings are made to contract by the working of the pulleys, and that while the observer at M sees one ring absorbed, the observer at T sees the graduated disk move by *n* divs. Then the value of the disk units in terms of the wave-length of sodium light can be found.

The glass surfaces (*a*, *b*) must not touch during these observations. If the surfaces be moved uniformly together the ring system expands at a uniform rate until they touch, when the system begins to expand at a very much slower rate. Thus we shall know the position of contact.

The burner was surrounded by an Argand chimney, and glass plates (not shown in the figure) were placed between it and the rest of the apparatus to cut off heat. It was found well to leave the apparatus for 15 minutes after lighting up, till temperature equilibrium was established; then the rings were fairly steady, and observations could be obtained.

At first the plan was to have one observer at the telescope and another at the microscope, as above described. But this was unsatisfactory, there being a want of cooperation between hand and eye; so a second pulley string (s_2 s_2) was fitted to pulley P_1 and passed round pulley P_2 so that the microscope observer could move the ring system himself, and when the observer at the telescope called out a reading to him he put it down. This method of working was retained as satisfactory.

Table IV. shows the results ultimately obtained. The rings moved to some extent under the temperature changes (though this movement was small when precautions were taken). But we know about the time taken to pass from ring to ring, and by measuring the time taken for the creep of one ring, we can make a correction. This is the use of column 1.

It will be seen that the four means agree very well, but

TABLE IV.

Calibration results for the apparatus, using the levers with the lowest (usual) ratio.

Numbers are expressed in a unit which is one hundred times the unit of the apparatus 10^{-7} cm.

Ring Creep.	No. of Rings.	Readings.	Diff.	Mean.	Ring Creep.	No. of Rings.	Readings.	Diff.	Mean.
1 ring in 60^{s} contract.	5	6·1	11·7	13·9 or for 1 ring 2·78	1 ring in 30^{s} contract.	10	23·1	27·2	27·7 or for 1 ring 2·77
		44·4	14·4				45·9	26·9	
		30 0	16·1				19·0	26·6	
		13·9	13·1				42·4	30·2	
		0·8	12·9				12·2	25·2	
		37·9	15·0				37·0	30·4	
		22·9	15·0				6·6	26·3	
		7·9	12·9				30·3	29·1	
		45·2	14·2				1·2	27·5	
		31·0					23·7		
1 ring in 40^{s} contract.	5	26·8	15·1	13·74 or for 1 ring 2·75		10	44·2	27·4	27·5 or for 1 ring 2·75
		11·7	11·9				16·8	26·5	
		49·8	12·5				40·3	27·8	
		37·3	14·8				12·5	27·6	
		22·5	15·0				34·9	28·9	
		7·5	11·9				5·0	26·3	
		45·6	13·5				29·7	27·8	
		32·1	15·0				1·9	27·1	
		17·1	14·0				24·8	27·9	
		3·1					46·9		

Mean of 5 rings $=13·82$. Mean of 10 rings $=27·60$.

Mean (of 270) for 1 ring $=2·76$.

Or, allowing for creep $=2·84$.

$$\therefore \frac{\lambda}{2}=284 \text{ units.}$$

$$\therefore 1 \text{ unit}=\frac{589}{2\times 284}\,\mu\mu=\mathbf{1·037}\,\mu\mu.$$

the individual values are not nearly so close ; surprise may be felt at the considerable discrepancies, for if the apparatus in its general use were not more reliable than in this calibration it would not be very efficient. But the conditions in the two cases are very different, for in calibration (1) the levers are uncovered ; (2) the burner being near causes considerable disturbances ; (3) to avoid a large creep during an observation the levers are moved much faster than usual, which may cause shaking.

The value obtained from calibration agreed closely with the number previously estimated by measurement of the lever-arms.

TABLE V.

Calibration results for the apparatus, using the levers in the middle and high ratios.

Ring Creep.	No. of Rings.	Readings.	Diff.	Ring Creep.	No. of Rings.	Readings.	Diff.
1 ring in 30^s contract.	1	36·2 9·8	26·4	None apparent.	5	23·5 40·0	33·5
	2	43·2 49·6	53·6		5	40·0 9·3	30·7
1 ring in 45^s contract.	2	49·9 17·3	52·6		5	9·3 27·1	32·2
	2	17·3 17·5	49·8		5	27·1 47·1	29·4
	2	17·5 14·6	52·9		5	47·7 13·6	34·1
					5	49·1 15·3	33·8
					5	15·3 32·5	32·8

1 ring (mean of 9) 26·2.

$$\therefore \frac{\lambda}{2}=2620 \text{ units.}$$

$$1 \text{ unit}=\frac{588}{2\times2620}\,\mu\mu.$$

$$=0{\cdot}112\,\mu\mu.$$

1 ring (mean of 35) 6·46.

$$\therefore \lambda=646 \text{ units.}$$

$$1 \text{ unit}=\frac{589}{2\times646}\,\mu\mu.$$

$$=0{\cdot}45\,\mu\mu.$$

The band system was disturbed by the passing of a cart in the streets, the disturbance being visible before any sound of the cart could be heard.

In every such case a delay was required.

The value determined for one disk unit is given at the bottom of Table IV.

Calibration work could not be done in the daytime; the working of a neighbouring factory caused a rythmic fluctuation of the ring system.

Table V. gives a rough calibration for the lever system when the bearings were so placed that the leverage was higher. Only approximate values were obtained, for these leverages were never used in actual measurements; but it was interesting to find values for the higher leverages and to see how nearly they agreed with one another.

The highest leverage position gives for the value of one disk-unit the value 0·1 $\mu\mu$, which is certainly small.

(3) *Diaphragm Movement.*

There are two distinct measurements involved :—

A. Observe the position of the diaphragm at rest by making the contact *ab* (fig. 2, p. 438), then draw away *a*, and pass a steady current through the receiver so as to move the diaphragm to a new position of rest; now move up *a* slowly towards the diaphragm, watching the graduated disk and listening for contact. Thus we can measure the movement of the diaphragm centre due to a steady current. This we can do for any current down to such small ones as cause a movement too minute for observation; then we shall have a relation between current in the telephone, and diaphragm displacements, between any desired limits of the current. Plot a curve for this relation.

B. Unscrew the telephone-holder from the apparatus, fit on an earpiece to it, and place the receiver in a circuit containing also a cell (whose E.M.F. is known), a resistance-box and a tapping-key, the receiver being shunted by another resistance-box.

If the ear is placed on the receiver when the key is released a sound is heard; this can be reduced in intensity by increasing resistance, or decreasing the shunt, until no sound is heard. Find the limit; this gives us the lower limit of audibility of sounds produced in this particular way as impulses. Observe the current used corresponding to the limit.

Now return to the curve obtained in A, and mark on it, by extrapolation, the current just found. This will give us the movement corresponding to the smallest audible sound impulse.

It must be observed that we are dealing with an impulse, for the diaphragm is released from a position of strain, vibrates for some time under considerable damping, and so soon comes to rest. In Section IV. an attempt is made to represent roughly the nature of the impulse in this special case.

The diaphragm in its vibration has its own particular frequency, and our determination refers to this frequency.

In all cases I measured my own limit of hearing (for both ears) so that the value obtained is probably somewhat low, as I have had considerable practice in listening to small telephone sounds.

So faint is the smallest sound that the observations were only possible in the dead of night.

Tables VI A., VII A., VIII A. give four complete sets of diaphragm readings.

Tables VI B., VII B., VIII B. give the corresponding currents for smallest sound-impulses.

TABLE VI A.

Showing Diaphragm movements for given steady currents. The same units for length and current as used previously.

Movement.	Mean.	Corr. Mean, $\mu\mu$.	Resistance and Current.	Movement.	Mean.	Corr. Mean, $\mu\mu$.	Resistance and Current.
0·02 0·02 0·03	0·027	2·8	75,000 ω. C=13·2	0·13 0·13 0·12	0·127	13·2	20,000 ω. C=50
0·03 0·03 0·03	0·03	3·1	60,000 ω. C=16·6	0·15 0·16 0·17	0·16	16·6	15,000 ω. C=66·6
0·03 0·04 0·03	0·033	3·4	50,000 ω. C=20.	0·20 0·25 0·22	0·22	22·9	10,000 ω. C=100
0·04 0·03 0·04	0·037	3·9	45,000 ω. C=22·2	0·40 0·38 0·38	0·387	40·3	5,000 ω. C=195
0·05 0·04 0·04	0·043	4·5	40,000 ω. C=25	0·55 0·50 0·60	0·55	57·2	3,000 ω. C=320
0·05 0·06 0·05	0·053	5·5	35,000 ω. C=28 6	1·30 1·25 1·20	1·28	133·0	1,000 ω. C=893
0·08 0·08 0·07	0·077	8·0	30,000 ω. C=33	2·00 1·90 1·90	1·93	201·0	500 ω. C=1660
0·10 0·10 0·10	0·100	10·4	25,000 ω. C=40	3·50 3·50 3·60	3·50	367·0	200 ω. C=3100

E.M.F.=1·430 V. constant.

TABLE VI B.

Readings of Steady Current corresponding to smallest audible impulse.

Main Resistance.	Shunt-Resistance.		Current.	Mean.
	Left Ear.	Right Ear.		
100,000 ω.	40 ω.	40 ω.	2·53	2·60
75,000 ω.	20 ω.	40 ω.	2·66	

TABLE VII A.

Similar to Table VI A.

Movement.	Mean.	Corr. Mean, $\mu\mu$.	Resistance and Current.	Movement.	Mean.	Corr. Mean, $\mu\mu$.	Resistance and Current.
0·01 0 02 0·03	0·02	2·1	75,000 ω. C=13·2	0 10 0·10 0·11	0·103	10·7	20,000 ω. C=50
0·03 0·02 0·03	0·027	2·8	65,000 ω. C=15·4	0·12 0·13 0·12	0·123	12·8	15,000 ω. C=66·6
0·03 0·04 0·04	0·037	3·9	50,000 ω. C=20	0·18 0·20 0·20	0·193	20·1	10,000 ω. C=100
0·05 0·04 0·05	0·043	4·5	45,000 ω. C=22·2	0·28 0·30 0·28	0·287	29·9	5,000 ω. C=195
0·06 0·05 0·05	0·057	5·9	40,000 ω C=25	0·40 0·40 0·38	0·393	40·9	3,000 ω. C=320
0·06 0·07 0·06	0·063	6·5	35,000 ω. C=28·6	1·20 1·10 1·20	1·17	122·0	1,000 ω. C=893
0·07 0·08 0·07	0·073	7·6	30,000 ω. C=33,3	2·20 2·22 2·20	2·21	230·0	500 ω. C=1860
0·08 0·09 0·08	0·077	8·0	25,000 ω. C=40	3·10 3·15 3·10	3·12	324·0	300 ω. C=2380

E.M.F.=1·430 V. constant.

TABLE VII B.

Similar to Table VI B.

Main Resistance.	Shunt-Resistance.		Current.
	Left Ear.	Right Ear.	
100,000 ω	40 ω	40 ω	2·53

Table VIII a.

Similar to Table VI a.

Movement.	Mean.	Corrected Mean, μμ.	Resistance and Current.	Movement.	Mean.	Corrected Mean, μμ.	Resistance and Current.
0·02 0·03 0·02	0·023	2·4	75,000 ω. C=13·2	0·09 0·10 0·10	0·097	10·1	25,000 ω. C=40
0·03 0·03 0·03	0·030	3·1	65,000 ω. C=15·4	0·12 0·13 0·12	0·123	12·8	20,000 ω. C=50
0·03 0·04 0·03	0·033	3·4	55,000 ω. C=18·2	0·20 0·20 0·20	0·200	20·8	10,000 ω. C=100
0·03 0·04 0·04	0·037	3·9	50,000 ω. C=20	0·30 0·32 0·28	0·300	31·2	5,000 ω. C=195
0·05 0·05 0·04	0·047	4·9	45,000 ω. C=22·2	0·50 0·50 0·47	0·49	51·0	3,000 ω. C=320
0·05 0·06 0·06	0·057	5·9	40,000 ω. C=25	1·30 1·35 1·40	1·35	140·0	1,000 ω. C=893
0·07 0·06 0·08	0·070	7·3	35,000 ω. C=28·6	3·10 3·10 3·20	3·13	325·0	300 ω. C=2380
0·08 0·09 0·08	0·087	9·0	30,000 ω. C=33·3				

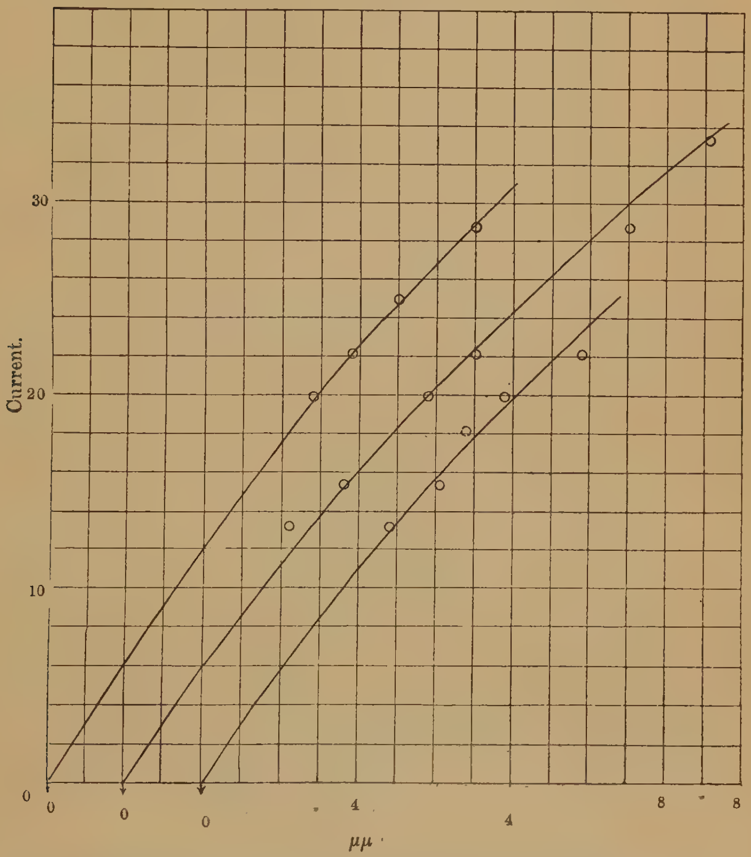
E.M.F.=1·430 V. constant.

Table VIII b.

Main Resistance.	Shunt Resistance.		Current.
	Left Ear.	Right Ear.	
100,000 ω.	40 ω.	40 ω.	2·53

The curves on fig. 4 are taken from VI A., VII A., VIII A. In these curves the points are not very uniformly distributed along the lines drawn; but this is natural, for the readings were taken for such small distances (3×10^{-7} centim. or so) that the apparatus in its present form was near the limit of its working power.

Fig. 4.

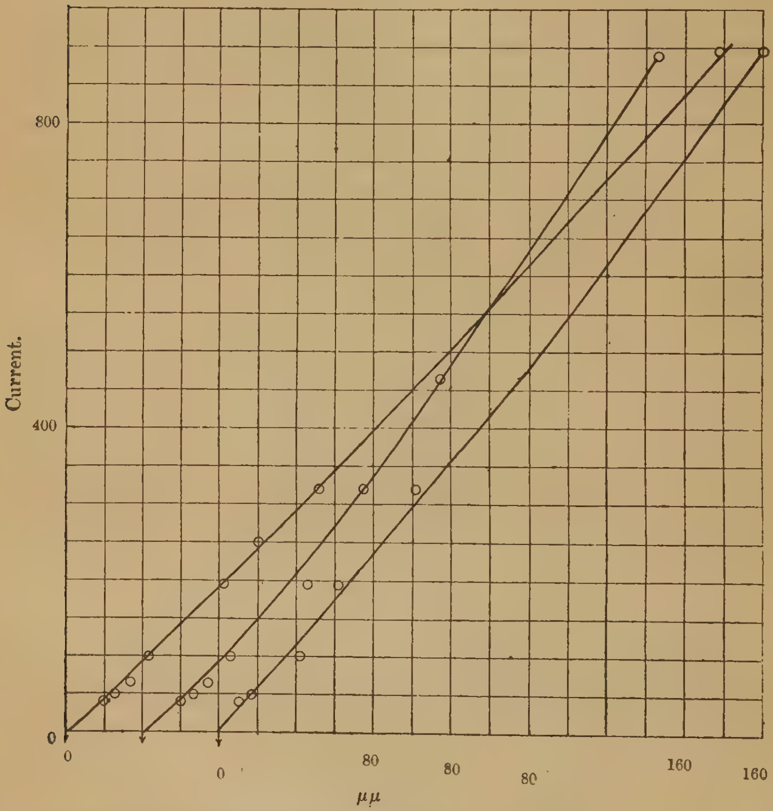


Extrapolation was used to arrive at the results; but it was not very hazardous extrapolation, since the curve is merely continued to the origin, through which it obviously passes. The values obtained from the curves agree very closely, the average being 0·37 μμ for the smallest audible impulse.

If this is taken as a true value, the amplitude for the continuous uniform vibration audible cannot be greater than 0·37 $\mu\mu$ and is probably less. Our value would seem to be a superior limit.

The Tables VI A., VII A., VIII A. furnish not only the curves on fig. 4 for small displacements (0–10 $\mu\mu$), but also those on fig. 5 for medium displacements (10–160 $\mu\mu$). Here the readings can be taken with greater percentage accuracy, and the points lie more uniformly along them.

Fig. 5.



That the curves are not parallel to one another and even cross, as in fig. 5, is not surprising, for the receiver is set up differently for each curve obtained, so that a small difference in the tightening of the diaphragm would make a difference in the ratio current/displacement, and so the general direction of the curve would be different.

In fig. 4 the curves will be seen to be concave to the line of abscissæ. Now it is obvious that for large currents the

TABLE IX A.

Similar to Tables VI., VII., VIII., but having larger diaphragm displacements.

Movement.	Mean.	Corr. Mean, μμ.	Throw.	Current and Resistance.	Movement.	Mean.	Corr. Mean, μμ.	Throw.	Current and Resistance.
0·70 0·70 0·75	0·72	75·0	1·30	2000 ω. C=472	12·0 12 05 11·95	12·0	1250·0	13·0	20 ω. C=7140
1·30 1·30 1·29	1·297	134·0	2·0	1000 ω. C=893	13·5 13·4 13·5	13·47	1397·0	......	10 ω. C=7690
2·50 2·60 2·50	2·53	263·0	3·40	500 ω. C=1610	51·2 52·0 50·5	51·2	5320·0	55·2	10 ω. C=30,760
5·3 5·4 5·3	5·33	554·0	6·8	200 ω. C=3125	52·8 52·0 53·0	52·6	5470·0	56·9	5 ω. C=32,000
7·5 7·5 7·7	7·37	767·0	8·3	100 ω. C=4540	54·0 54·5 54·5	54·3	5650·0	57·5	2 ω. C=32,800
9·8 9·9 9·8	9·83	1020·0	10·5	50 ω. C=5880					

E.M.F. { First six sets .... 1·430 V. constant.
Last three sets ...... 5·900 V. constant.

TABLE IX B.

Kind of Impulse.	Volts.	Main Resistance.	Cell Resistance.	Current.
Begins to be comfortably loud	1·43	10,000 ω.	2 ω.	100
,, ,, uncomfortably loud ...	1·43	100 ω.	2 ω.	4,500
,, ,, unbearable...............	6·0	5 ω.	8 ω.	30,800

Table X a.

Similar to Table IX.

Movement.	Mean.	Corrected Mean, $\mu\mu$.	Throw.	Corrected Throw, $\mu\mu$.	Current and Resistance.
0·90 0·93 0·95	0·93	97·0	1·25	130·0	10,000 ω. C=400
1·25 1·25 1·30	1·27	132·0	2·00	208·0	5,000 ω. C=780
3·50 3·55 3·45	3·50	364·0	4·7	489·0	2,000 ω. C=1890
6·25 6·20 6·30	6·25	650·0	9·0	936·0	1,000 ω. C=3570
11·9 11·8 11·7	11·8	1230·0	18·7	1940·0	500 ω. C=6440
31·0 31·3 31·3	31·2	3245·0			100 ω. C=18,200
40·0 40·5 39·7	40·0	4160·0			50 ω. C=23,500
51·8 52·4 52·5	52·0	5460·0			5 ω. C=32,000

E.M.F.=5·90 V. constant.

Table X b.

Kind of Impulse.	Volts.	Main Resistance.	Cell Resistance.	Current.
Begins to be comfortably loud	5·90	10,000 ω.	8 ω.	410
,, ,, uncomfortably loud...	5·90	400 ω.	8 ω.	7,700
,, ,, unbearable	5·90	5 ω.	8 ω.	30,300

curve will be convex in the above sense, and we might reasonably expect it to be so throughout the curves to the origin. But if the curve when very near the origin has a point of flexure as supposed, we see the importance of plotting the curve in this region so as to obtain its true shape.

This peculiarity might arise from (1) a "buckle" in the diaphragm; (2) irregularities in the field. But we have no data for deciding between these various speculations.

From the data obtained it is possible to draw up roughly a scale of loudness, thus:—

(1)	Begins to be audible	0·4	$\mu\mu$
(2)	,, ,, comfortably loud	50	,,
(3)	,, ,, uncomfortably loud	1000	,,
(4)	,, ,, overpowering	5000	,,

We need standards of loudness corresponding to our system of standards of light-intensity. (2), (3), and (4) are only meant to be rough indications, but (1) (which is a direct test of the limit of hearing and does not involve the observer's personal judgment of loudness) is much more important. The values for it agree well together*.

(4) *The Damping of the Diaphragm.*

In Section III. a measurement is made of sound-impulses. It is interesting, therefore, to know the nature of these impulses, *i.e.* the extent to which the vibrations are damped.

We proceed thus:—(1) Measure the position (a) of the contact of the telephone when no current is passing in it. (2) Pass a current in the telephone so as to draw the diaphragm away from contact, then measure the new contact-position (a_0). (3) Draw away the contacts, and then stop the current; the diaphragm will be released and will just make contact if we arrange the pointer aright; measure this contact-position (a_1).

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* A. Franke (see Proc. Soc. Tel. Eng. vol. xvi.) made a determination of the amplitude of a diaphragm for the smallest sound audible. The value obtained was 1·2 $\mu\mu$. But whereas it refers to a continuous sound, the value obtained by the author refers to a sound-impulse. The method of Franke was an interference optical one, and the smallest measured displacement was 52 $\mu\mu$; also he seems to have trusted to having a straight line from that point to the origin.

Cross & Mansfield (Proc. Amer. Acad. vol. xx. 1893) summarize the work which had been done on this value.

It is to be understood that a_0 and a_1 and a_n are displacements from the normal position a; then $\frac{a_1}{a_0} = \rho$ is the damping factor for one $\frac{1}{2}$ vibration.

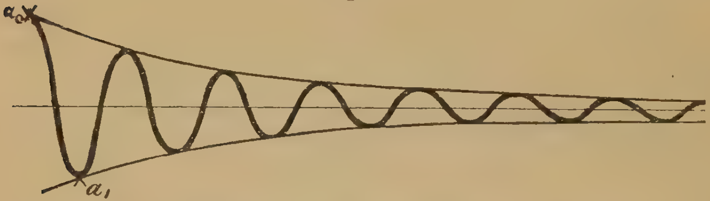
For a few vibrations it seems fair to assume for our purposes that ρ does not alter much.

Then we have for the position after n half-vibrations,

$$\left(\frac{a_1}{a_0}\right)^n . a_0 = a_n.$$

On this basis plot a curve for the impulse (fig. 6).

Fig. 6.



From ten observations on small distances the mean value for ρ was approximately $\frac{5}{6}$.

Besides the work above indicated, many other measurements were made, viz.: (1) microphone action of various substances; (2) the movement of the receiver-diaphragm when in circuit with a transmitter in action; (3) apparent coherence of the surfaces under certain conditions.

These applications will be reserved at present.

SUMMARY.

The main purpose of this paper is to show:—

(1) That this method of measuring small distances by electric contact is reliable.

(2) That, whereas in other methods for measuring small distances a limit to working is made by the size of some wave-length, in this method the limit is far lower, is not thus dependent, and has not been reached in the apparatus so far made.

(3) That a measurement can be made of the smallest audible impulsive sound given by a telephone-diaphragm.

(4) The method will probably have many other applications, where small measurements are involved.

I wish to thank Mr. W. H. Everett, B.A., B.E., for some valuable suggestions, and Professor W. H. Heaton, M.A., for his kind interest in this research.

DISCUSSION.

Prof. EVERETT expressed his interest in the delicacy of the system of measurement, and asked if the micrometer had been used to determine the form of the plate when vibrating.

Mr. PHILLIPS asked if experiments on the smallest sound audible had been made on different people, as it would be physiologically interesting to know if this minimum value were constant.

Mr. CAMPBELL asked if the sound was expected when heard.

Mr. SHAW said he had not conducted experiments on the form of the plate when vibrating, although he had investigated its law of damping. He said the small sounds were expected, and the limit varied.

Prof. AYRTON said he found it easy to rid galvanometers and electrometers from extraneous disturbance by placing them on a block of stone resting on a thickness of 3 or 4 feet of slag-wool contained in a hollow brick pillar.

XXIX. *On the Viscosities of Mixtures of Liquids and of Solutions.* *By* Charles H. Lees, *D.Sc.*[*]

In recent years many determinations of the viscosities of mixtures of liquids and of solutions have been made in the endeavour to discover the law of connexion of the viscosity of a mixture with the relative amounts and viscosities of its constituents. As a result several empirical formulæ have been proposed which represent the observations with more or less accuracy. Of these formulæ, the one first used by Arrhenius in 1887, and since then by Reyer, Wagner, Lauenstein, and Kanitz, for weak salt-solutions or for mixtures of liquids when one liquid is present to the extent of 90 per cent. or more, seems to be the most valuable. According to it the viscosity η at a temperature t, of a mixture which contains in 1 c.c., v_1 c.c. of a liquid of viscosity η_1, v_2 c.c. of one of viscosity η_2, &c., at temperature t, is given by the equation

$$\eta=\eta_1^{v_1}\,.\,\eta_2^{v_2}\,.\,\eta_3^{v_3}\,.\,.\,.\,.\,.$$

or

$$\log\eta=v_1\log\eta_1+v_2\log\eta_2+v_3\log\eta_3+\,.\,.\,.\,.\,.$$

so long as one constituent is present to the extent of 90 per cent. or more. It is the object of the present paper to consider whether this formula can be supported on theoretical grounds, to see how far it agrees with the observed facts for mixtures generally, and if the agreement is unsatisfactory to replace it by a more suitable expression.

To arrive at a theory for mixtures of fluids which have no chemical action on each other, we may suppose the volume of a mixture to be divided into elementary volumes by, say, three series of parallel planes. Each of these elementary volumes we may suppose occupied exclusively by one constituent. The limit of the calculated viscosity of a medium so built up when the elementary parts are taken indefinitely small, may be taken as the viscosity of the mixture.

The fundamental equation of the theory of viscosity of a fluid is $F=\eta\,.\,\frac{dv}{dx}$, where dv is the difference of the parallel velocities of two plane layers of fluid situated at a distance dx apart, F is the tangential force transmitted through an area of 1 sq. cm. between the layers and parallel to them, and η is the viscosity of the fluid.

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[*] Read June 8, 1900.

If the motion throughout the fluid is steady and parallel to the y axis, and there is no variation of it along that axis, the equation

$$\frac{\partial^2 v}{\partial x^2}+\frac{\partial^2 v}{\partial z^2}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

must hold throughout the fluid. At a surface of separation of two fluids of viscosities η_1 and η_2, if there is neither chemical action nor slipping, we must have

$$v_1=v_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

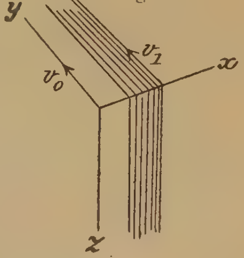
and

$$\eta_1\frac{\partial v_1}{\partial n}=\eta_2\frac{\partial v_2}{\partial n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where v_1 and v_2 are the velocities close to the surface in the two fluids, and dn is an element of the normal to the surface. At a solid surface touched by a fluid there must be no relative motion of solid and fluid.

These are the necessary and sufficient conditions for the solution of any "plane" problem on the motion of viscous fluids, and the difficulty of finding a solution in any special case is a mathematical one which increases with the number of different fluids present in the space considered, and the complexity of their lines of separation. We proceed to consider a few simple stable arrangements of the fluids for which the solutions can be readily obtained.

Fig. 1.



I. Taking the velocity throughout parallel to the y axis, let us assume that it is independent of z, equal to v_0 throughout the plane $x=x_0$, and to v_1 throughout the plane $x=x_1$, and that the surfaces of separation of the various fluids present between those planes, are the planes $x=x_2$, x_3, &c.

If there are only two fluids of viscosities η_1 and η_2 present in equal volumes (fig. 1), the equations (1), (2), and (3) above, give for the viscosity η of the mixture,

$$\frac{1}{\eta}=\frac{1}{2}\left(\frac{1}{\eta_1}+\frac{1}{\eta_2}\right).$$

If each c.c. of the mixture contains v_1 c.c. of the first medium and v_2 of the second, then

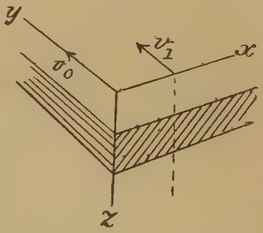
$$\frac{1}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2}.$$

In the general case where v_1, v_2, v_3, &c. c.c. of the constituents η_1, η_2, η_3, &c. are present in 1 c.c. of the mixture

$$\frac{1}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2} + \frac{v_3}{\eta_3} + \ldots$$

This result is independent of the number of layers of each constituent present. In the tables which follow it will be referred to as the "mobility formula."

Fig. 2.



II. Making the same assumptions as to the velocities, but taking the planes separating the fluids as $z = z_0, z_1, z_2$, &c., if the fluids are present in equal volumes (fig. 2) we have

$$\eta = \tfrac{1}{2}(\eta_1 + \eta_2);$$

if 1 c.c. contains v_1 volumes of the first and v_2 of the second

$$\eta = v_1\eta_1 + v_2\eta_2,$$

and in the general case

$$\eta = v_1\eta_1 + v_2\eta_2 + v_3\eta_3 + \ldots.$$

A result again independent of the number of layers of each constituent present. In the following pages this will be referred to as the "viscosity formula."

III. Thirdly, let there be two systems of separating planes mutually perpendicular to each other.

If there are two fluids of viscosities η_1, η_2 present in equal volumes, distributed as shown in fig. 3, or in fig. 4, the solution of the equations (1), (2), (3) above, for this case gives for the viscosity η

$$\log \eta = \tfrac{1}{2}(\log \eta_1 + \log \eta_2).$$

If 1 c.c. of the mixture contains v_1 c.c. of the η_1 and v_2 c.c. of the η_2 constituent

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2.$$

For a mixture containing in 1 c.c. v_1, v_2, v_3, &c. c.c. of media of viscosities η_1, η_2, η_3, &c.*

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2 + v_3 \log \eta_3 + \ldots .$$

This result is independent of the number of the elementary prisms of each constituent present. In the tables which follow this will be referred to as the "logarithmic formula."

Fig. 3.

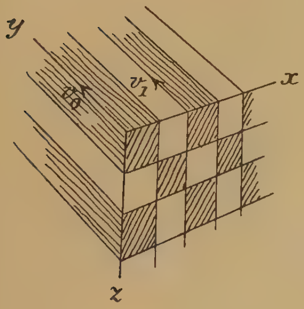
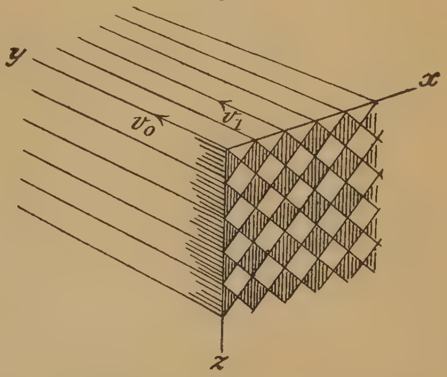


Fig. 4.



The number of mixtures of liquids, of which the viscosities have been observed and are available for comparison with the results of theory, is small, and some of them, for which the observed values of the viscosities do not fall within those of the constituents, *e.g.* mixtures of water and alcohols or certain acids †, are seen to be outside the limits of the above theory. Of the rest some, *e.g.* chloroform or carbon bisulphide and ether ‡, have points of inflection on the curve connecting viscosity and constitution, and of such singularities none of the above formulæ can take account. The conclusion may at once be drawn that the viscosity of a mixture of liquids is in general not dependent solely on the viscosities and amounts of the constituents present, but is influenced by some other action of which none of the above theories takes account. Notwithstanding this fact, it may be of use in the case of mixtures in which the action of this unknown disturbing effect appears to be least, to compare the values given by the three

* Lees, Phil. Mag. xlix. p. 225 (1900).

† Wijkander, Wied. *Ann. Beibl.* iii. p. 8 (1879); Thorpe & Rodger, J. Chem. Soc. lxxi. p. 367 (1897).

‡ Traube, *Ber. Chem. Ges.* xix. p. 871 (1886); Pagliani & Battelli, *Ann. R. Ist. Torino*, xiii. p. 37 (1885).

formulæ with those found by experiment; and in the following Tables these observed values are compared with the values calculated from the recorded percentage compositions by weight, and the densities, on the assumption that no contraction occurs on mixing.

Thorpe and Rodger's Experiments *.

Carbon Tetrachloride and Benzine, at 60° C.

Per cent. Benzine.		Viscosity.						
			Calculated.					
Weight.	Volume.	Observed	Viscosity formula.	p. cent. error.	Logarithmic formula.	p. cent. error.	Mobility formula.	p. cent. error.
0	0	·00582						
22·4	34·0	503	·00517	+3	·00508	+1	·00497	−1
43·8	58·5	456	470	3	463	2	452	−1
67·7	79·2	422	431	2	425	1	420	−1
100	100	391						

Methyl Iodide and Carbon Bisulphide, at 0° C.

Per cent. Bisulphide.								
0	0	·00592						
21·6	33·2	518	·00538	+4	·00532	+3	·00526	+1
38·8	53·4	482	504	5	498	3	490	2
48·1	62·5	469	489	4	484	3	478	2
68·1	79·4	449	461	3	458	4	454	1
82·4	89·4	438	445	2	444	1	442	1
100	100	429						

The character of the results is unaltered if the comparison is made with the values given by Thorpe and Rodger for other temperatures.

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* Journ. Chem. Soc. lxxi. p. 360 (1897).

LINEBARGER'S EXPERIMENTS *.

Ethyl Ether and Benzine, at 25° C.

Per cent. Benzine.		Viscosity.						
			Calculated.					
Weight.	Volume.	Observed	Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·00230						
28·6	25·2	282	·00323	+18	·00293	+4	·00273	−3
56·9	52·6	362	424	17	380	5	340	6
75·7	72·4	438	497	14	459	5	415	5
100	100	599						

Carbon Bisulphide and Benzine, at 25° C.

Per cent. Benzine.								
0	0	·00358						
8·9	12·2	376	·00387	+3	·00380	+1	·00377	0
34·9	43·3	446	462	4	447	0	433	−3
75·9	81·7	544	555	2	545	0	535	−2
100	100	599						

Nitrobenzine and Benzine, at 25° C.

Per cent. Benzine.								
0	0	·001834						
14·4	18·8	1417	·001602	+13	·001486	+5	·001323	−7
37·6	45·2	1017	1277	25	1104	8	950	6
80·1	84·6	681	790	16	711	4	668	2
100	100	599						

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* Amer. Journ. Sc. ser. 4, vol. ii. p. 331 (1896).

Linebarger's Experiments (*continued*).

Ethyl Benzoate and Toluene, at 25° C.

Per cent. Toluene.		Viscosity.						
			Calculated.					
Weight.	Volume.	Observed	Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·01954						
15·3	18·1	1495	·001598	+7	·001549	+4	·001324	−1
47·3	52·4	939	1223	30	995	6	822	12
76·2	79·6	679	827	22	701	3	632	7
100	100	539						

Turpentine and Toluene, at 25° C.

Per cent. Toluene.								
0	0	·01343						
6·8	6·8	1192	·001288	+8	·001262	+6	·001219	+2
20·65	20·7	978	1177	20	1112	14	1026	5
53·7	53·8	701	911	30	822	17	745	6
75·1	75·1	607	739	21	678	12	633	4
100	100	539						

Acetic Ether and Nitrobenzine, at 25° C.

Per cent. Nitrobenzine.								
0	0	·00434						
22·9	18·1	582	·00687	+18	·00562	−3	·00504	−13
56·1	48·8	889	1117	26	875	2	692	22
75·5	69·7	1204	1410	17	1183	2	928	15
100	100	1834						

Linebarger's Experiments (*continued*).

Carbon Bisulphide and Toluene, at 25° C.

Per cent. Toluene.		Viscosity.						
			Calculated.					
Weight.	Volume.	Observed	Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·00358						
7·3	10·3	370	·00377	+2	·00373	+1	·00372	+1
40·0	48·5	417	447	7	438	5	429	3
63·2	71·5	469	489	4	481	3	472	1
100	100	541						

Carbon Bisulphide and Ether, at 25° C.

Per. cent. Ether.								
0	0	·00358						
13·1	21·1	338	·00331	−2	·00326	−4	·00321	−5
34·4	48·2	306	296	3	289	6	282	8
62·8	75·0	269	262	3	257	5	253	6
100	100	230						

Chloroform and Carbon Tetrachloride, at 25° C.

Per cent. Carb. Tetrachl.								
0	0	·00540						
19·3	18·2	569	·00602	+6	·00590	+4	·00581	+2
57·3	55·6	659	731	11	710	8	690	5
81·2	80·1	761	815	7	800	5	787	3
100	100	883						

Several mixtures of liquids having nearly equal viscosities were investigated by Linebarger, but are not given here, as the differences between the values calculated by the three formulæ are in such cases too small to warrant conclusions as to the relative merits of the three being drawn.

WIJKANDER'S EXPERIMENTS *.

Benzine and Aniline, at 25° C.

Per cent. Aniline.		Viscosity.						
Weight.	Volume.	Observed	Calculated.					
			Vis. formula.	p. cent. error.	Log. formula.	p. cent. error.	Mob. formula.	p. cent. error.
0	0	·0065						
20	17·6	84	·0132	+57	·0091	+8	·0076	−9
50	46·1	138	241	75	158	14	107	22
80	77·4	271	361	33	289	7	193	29
100	100	447						

Ether and Alcohol, at 25° C.

Per cent. Alcohol.								
0	0	·00258						
25	23·7	360	·00499	+39	·00377	+5	·00317	−12
50	48·3	537	749	39	558	4	420	22
75	73·7	824	1009	22	838	7	625	24
100	100	1275						

Ether and Carbon Bisulphide, at 25° C.

Per cent. Carb. bisulph.								
0	0	·00258						
12·5	7·5	269	·00266	−1	·00265	−1	·00264	−2
25	16·1	276	276	0	274	1	271	2
50	36·5	299	299	0	294	2	290	3
66·7	53·5	320	318	−1	313	2	308	4
100	100	370						

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* Wied. *Ann.* Bd. iii. p. 8 (1879).

Wijkander's Experiments (*continued*)

Benzine and Alcohol, at 25° C.

P. cent. Alcohol.		Viscosity.						
			Calculated.					
Weight.	Vol.	Obs.	Vis. forml.	p. cent. error.	Log. forml.	p. cent. error.	Mob. forml.	p. cent. error.
0		·00641						
50	53·0	832	·00977	+17	·00923	+11	·00870	−5
100		1275						

An examination of these tables shows that no one of the three formulæ represents correctly the variation of the viscosity with constitution in every case. The most unsatisfactory of the three is that which makes the viscosity a linear function of the constitution, and of the other two that which makes the logarithm of the viscosity follow the linear law seems somewhat less unsatisfactory than the one which makes the mobility follow that law. In general the observed viscosity is less than that given by the logarithmic and greater than that given by the mobility law, *i. e.* the constitution shown in fig. 3 or 4 gives too great, and that in fig. 1 too small a value for the viscosity. If the observed values for different mixtures divided the interval between these two calculated values in some fairly constant ratio, it would have justified the conclusion that the viscosity of a mixture was a definite function of the amounts and viscosities of the constituents present, but it will be seen from the tables that the observed values are to be found in a different part of the interval for each mixture, and for some even outside it. Hence, even in mixtures of liquids which are generally understood to have no chemical action on each other, *i. e.* to be physical mixtures purely, there is some interaction of the liquids which prevents the viscosity of the mixture being a function of the amounts and viscosities of its constituents only.

In those cases where the observed viscosity is less than that calculated for fig. 3 or 4, a reduction of the calculated value might be made by assuming that there is a finite slip at each surface of contact of the two constituents. The viscosity would then diminish as the size of each element of the pattern of fig. 3 or 4 was decreased, and we should have some approach to the known fact that the viscosity in general decreases as we go from liquids with larger to liquids with smaller molecules. If we may take the molecular volumes of the liquids of the preceding tables as indications of the magnitude of the component parts of the pattern of figs. 3 and 4, the tables show no evidence of this decrease of viscosity for mixtures of liquids with small molecular volumes: in fact one of the most marked cases of small viscosity is that of turpentine and toluene, both with comparatively large molecular volumes; and in neither case would it be legitimate to assume that the molecules had dissociated.

Those cases in which the observed viscosities are higher than the normal can be more easily accounted for by some kind of loose chemical combination or "association" of the two constituents. The case of acetic ether and nitrobenzine may be instanced. Here there is a contraction of ·8 per cent. for a 50 per cent. by volume mixture, which shows that some action has taken place, and the viscosity is greater than in a normal mixture.

The experiments of Arrhenius [*], which enabled him to establish the logarithmic law as an empirical law, were made on aqueous solutions of alcohols and other substances of concentrations not exceeding about 10 per cent., and Reyer [†] found that the law held for aqueous solutions of acids. From what precedes it will be seen that in these cases, if the observed value of the viscosity of a 10 per cent. mixture is used to calculate by means of the formula that of a 5 per cent. mixture, and this value compared with the one found by experiment, the range over which the law is tested is too limited to furnish a sufficient test of its generality, and the deviations from it found in the above tables would not make themselves evident.

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[*] Arrhenius, *Zeitsch. für phys. Chem.* i. p. 285 (1887).

[†] Reyer, *ibid.* ii. p. 744 (1888).

For salt-solutions in which the concentration does not exceed 10 per cent., Arrhenius *, Reyer †, Wagner ‡, Lauenstein §, and Kanitz ‖ have found that the logarithmic formula applies. Brückner ¶ has found that the formula which makes the viscosity a linear function of the concentration applies; and Mützel ** uses a formula which introduces an additional unknown constant for each mixture.

It is therefore necessary to turn to stronger solutions for a comparative test of the three formulæ corresponding to the three models of a mixture represented at the beginning of this paper. The only available observations are those of Burkhard quoted in Landolt and Bornstein's Tabellen (2nd edition, p. 294) ††.

Sugar Solution at 20° C.

P. cent. Sugar.			Specific Viscosity.						
				Calculated.					
Weight.	Vol.	p. cent. of 30 % Sol.	Obs.	Vis. forml.	p. cent. error.	Log. forml.	p. cent. error.	Mob. forml.	p. cent. error.
0	0	0	1·0						
5	3·2	15·1	1·15	1·31	+14	1·18	+3	1·11	−4
10	6·5	30·6	1·33	1·63	23	1·41	6	1·26	5
15	9·9	46·5	1·56	1·96	26	1·68	8	1·46	6
20	13·5	63·4	1·89	2·31	22	2·04	8	1·75	7
25	17·2	80·8	2·35	2·67	14	2·47	5	2·20	6
30	21·3	100	3·07						

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[*] *Loc. cit.*

[†] *Loc. cit.*

[‡] *Zeitsch. für phys. Chem.* v. p. 31 (1890).

[§] *Ibid.* ix. p. 417 (1892).

[‖] *Ibid.* xxii. p. 336 (1897).

[¶] *Ann. der. Phys.* xlii. p. 287 (1891).

[**] *Ibid.* xliii. p. 15 (1891).

[††] Since this was written the observations of Hosking have been published (Phil. Mag. xlix. p. 274, 1900) and are considered pp. 475, 476.

As was found in the case of most of the mixtures of liquids, the linear viscosity law gives much too high, the logarithmic law somewhat too high, and the mobility law somewhat too low values for the viscosity.

The failure of the three formulæ deduced theoretically on the assumption that the constituents of a mixture are distributed as shown in figs. 1, 2, 3, and 4 respectively, to express the results of observations, leads one to attempt to find an empirical formula capable of so doing. As the deviations from the three formulæ are found to be different in different mixtures, it is evident that any such formula will involve an additional constant depending on the particular mixture considered.

The forms of the above three formulæ :—

$$\eta = v_1\eta_1 + v_2\eta_2,$$

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2,$$

$$\frac{1}{\eta} = v_1\frac{1}{\eta_1} + v_2\frac{1}{\eta_2},$$

suggest immediately the empirical formula :—

$$\eta^n = v_1\eta_1{}^n + v_2\eta_2{}^n,$$

where n is a constant to be determined for each mixture. In the following tables the values of n are given and the calculated and observed values of η for various mixtures are compared *.

Carbon Tetrachloride and Benzine at 60° C. $n = -{\cdot}42$.

Per cent. Benzine by volume.	Observed η.	Calculated η.
0	·00582	·00582
34·4	503	502
58·5	456	456
79·2	422	422
100	391	391

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* In most of the cases which follow no attempt has been made to determine n to a greater degree of accuracy than 2 or 3 units in the second decimal place.

Ethyl Ether and Benzine at 25° C. $n = -{\cdot}50$.

Per cent. Benzine by volume.	Observed η.	Calculated η.
0	·00230	·00230
25·2	282	282
52·6	362	361
72·4	438	438
100	599	599

Nitrobenzine and Benzine at 25°. $n = -{\cdot}50$.

Per cent. Benzine by volume.	Observed η.	Calculated η.
0	·01834	·01834
18·8	1417	1410
45·2	1017	1020
84·6	681	689
100	599	599

Ethyl Benzoate and Toluene at 25°. $n = -{\cdot}30$.

Per cent. Toluene by volume.	Observed η.	Calculated η.
0	·01954	·01954
18·1	1495	1489
52·4	939	938
79·6	679	676
100	539	539

Benzine and Aniline at 20° C. $n = -{\cdot}33$.

Per cent. Aniline by volume.	Observed η.	Calculated η.
0	·0065	·0065
17·6	84	85
46·1	138	138
77·4	271	259
100	447	447

Ether and Alcohol at 20° C. $n = -\cdot 11$.

Per cent. Alcohol by volume.	Observed η.	Calculated η.
0	·00258	·00258
23·7	360	368
48·3	537	538
73·7	824	812
100	1275	1275

The success of the attempt to represent the viscosities of these mixtures by means of the formula proposed, leads to the attempt being extended to mixtures of glycerine and water, in which the range of viscosity is very great. The following results have been obtained :—

Glycerine and Water at 8°·5 C. (Schöttner) *.
$n = -\cdot 22$.

Per cent. Glycerine.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·0136	·0136
49·8	43·9	·0925	·099
64·0	58·4	·222	·245
75·0	70·3	·552 †	·61
80·3	76·3	1·021	1·05
89·9	86·5	3·553	3·16
94·5	93·1	7·437	7·59
100	100	23·98 †	23·98

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* *Wien. Ber.* ii. 79, p. 477 (1879).

† Calculated from Schöttner's numbers.

Glycerine and Water at 20° C. (Archbutt & Deeley)*.
$n = -{\cdot}25$.

Per cent. Glycerine.		Per cent. of 97·5 per cent. Glycerine by volume.	Viscosity.	
By weight.	By volume.		Observed.	Calculated.
0	0	0	·0103	·0103
40·0	34·5	35·4	·038	·040
71·0	66·0	67·6	·236	·253
78·8	74·6	76·5	·498	·518
82·4	78·7	80·8	·75	·76
85·5	82·4	84·5	1·11	1·09
94·0	92·5	94·9	4·08	3·92
98·0	97·5	100	8·69	8·69

Applying the formula to the sugar and the sodium-chloride solutions investigated by Hosking †, and to the sugar solution tested by Burkhard, we have the following results:—

Sugar Solution at 0° C. (Hosking). $n = -{\cdot}50$.

Per cent. Sugar.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·0179	·0179
5	3·2	205	207
10	6·5	244	244
20	13·5	372	366
40	29·3	·1476	·1476

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* 'Lubrication and Lubricants,' London, Griffin, 1900, p. 133.

† Phil. Mag. xlix. p. 286 (1900).

Sugar Solution at 40° C. $n = -{\cdot}50$ (Hosking).

Per cent. Sugar.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·00657	·00657
5	3·2	732	742
10	6·5	843	848
20	13·3	1180	1170
40	29·3	3132	3132

Sugar Solution at 80° C. $n = -{\cdot}50$.

0	0	·00360	·00360
5	3·2	399	400
10	6·5	448	448
20	13·5	586	588
40	29·3	1288	1288

Sodium Chloride Solution at 0° C. (Hosking). $n = -3{\cdot}0$.

Per cent. Sodium Chloride.		Viscosity.	
Weight.	Volume.	Observed.	Calculated.
0	0	·0179	·0179
5	2·44	186	189
10	5·03	204	204
20	10·64	267	267

Sodium Chloride Solution at 40° C. $n = -{\cdot}33$.

0	0	·00657	·00657
5	2·44	725	724
10	5·03	802	805
20	10·64	1025	1025

Sodium Chloride Solution at 80° C. $n = {\cdot}25$.

0	0	·00360	·00360
5	2·44	399	402
10	5·03	455	451
20	10·64	571	571

Sugar Solution at 20° C. (Burkhard).

$n = -.50$.

Per cent. Sugar.		Per. cent of 30 per cent. Solution.	Viscosity.	
Weight.	Volume.		Observed.	Calculated.
0	0	0	1·0	1·0
5	3·2	15·1	1·15	1·14
10	6·5	30·6	1·33	1·33
15	9·9	46·5	1·56	1·56
20	13·5	63·4	1·89	1·89
25	17·2	80·8	2·35	2·34
30	21·3	100	3·07	3·07

The agreement between the calculated and experimental values in all the above cases is sufficient to justify the use of the empirical formula

$$\left(\frac{1}{\eta}\right)^m = v_1\left(\frac{1}{\eta_1}\right)^m + v_2\left(\frac{1}{\eta_2}\right)^m$$

as, at any rate, a first approximation towards a representation of the viscosity of a physical mixture in terms of the viscosities and natures of its constituents. Like other empirical formulæ, it will in time be replaced by a formula founded on theory and capable of including cases in which the liquids, owing to some chemical action on each other, give rise to mixtures having viscosities outside the limits of those of their constituents.

Since a liquid at temperature t may be regarded as produced by a mixture of suitable amounts of the liquid at temperatures 0 and t_1 respectively, the above formula for the viscosities of mixtures should be capable of expressing the variation of the viscosity of a liquid with temperature.

If 1 c.c. of a mixture at temperature t is supposed to result from mixing v_0 c.c. of liquid at 0° C. and v_1 c.c. of liquid at t_1° C., $t = v_1 t_1$; and if the viscosity is η_0 at 0° C., η at t° C., and η_1 at t_1° C., then

$$\left(\frac{1}{\eta}\right)^m = v_0\left(\frac{1}{\eta_0}\right)^m + v_1\left(\frac{1}{\eta_1}\right)^m$$

$$= \left(\frac{1}{\eta_0}\right)^m + \left\{\left(\frac{1}{\eta_1}\right)^m - \left(\frac{1}{\eta_0}\right)^m\right\}\frac{t}{t_1}$$

$$= \left(\frac{1}{\eta_0}\right)^m \{1+\alpha t\},$$

where

$$\alpha = \frac{1}{t_1}\left\{\left(\frac{\eta_0}{\eta}\right)^m - 1\right\}.$$

Hence

$$\eta = \frac{\eta_0}{(1+\alpha t)^{\frac{1}{m}}},$$

an empirical formula proposed by Slotte [*], and found by him, and more extensively by Thorpe and Rodger [†], to be applicable to all liquids on which experiments have been made.

The values of m for most of the mixtures mentioned in the preceding tables vary between ·20 and ·50; and Thorpe and Rodger have found its values in Slotte's temperature-variation formula to lie between ·22 and ·3 for alcohols, and to be about ·6 for water, benzine, ether, and chloroform. In the following table (p. 479) the values found suitable for expressing the viscosity of a mixture in terms of the viscosities of its constituents, are compared with those found best for expressing the variation of the viscosity of each constituent with temperature.

Although in the examples of non-electrolytic mixtures and solutions there seems to be some connexion between the values of m in the formula for the temperature-variation of the viscosities of two liquids, and its value in the formula for the viscosities of mixtures of the two, the number of instances is too small to warrant a general conclusion being drawn. In the case of the electrolytic solution (NaCl) the values of m for the mixtures at different temperatures vary greatly from one another, although the values in the temperature formula are practically identical. Possibly the magnitude of the heat of

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[*] *Ofv. Finska Vet. Soc. Förhand.* xxxii. p. 127, formula (11) (1890).

[†] Phil. Trans. A. 189. p. 96 (1897).

Liquids.	Values of *m*.		
	In Temperature Variation Formula.		In Mixture Formula.
Carbon Tetrachloride and Benzine	·58 *	·64 *	·49
Nitrobenzine and Benzine	·67 †	·64	·50
Ethyl Ether and Benzine........	·68	·64	·50
Ethyl Ether and Alcohol..................	·68	·23	·11
Ethyl Benzoate and Toluene	·50 ‡	·61	·30
Glycerine and Water	·12 §	·65	·22 & ·25
40-per-cent. Sugar solution and water.	·45 ‖	·65	·50
20-per-cent. NaCl solution and water...	·66 ‖	·65	3·0 to −·25

* The numbers in these two columns, with the exception of those for nitrobenzine, ethyl benzoate, and glycerine, are taken from Thorpe and Rodger's papers.

† Calculated from observations of Pribram and Handl, *Wien. Ber.* II. lxxviii. p. 113.

‡ Calculated from observations of Rellstab, *Inaug. Diss.* Bonn, 1868.

§ Calculated from Schöttner's values, *l. c.*

‖ Calculated from Hosking's values, *l. c.* The agreement between observed and calculated values may be seen from the following tables:—

40-per cent. Sugar Solution.

Temperature	Viscosity.	
	Observed.	Calculated.
0° C.	·148	·148
10	·895	·903
20	·607	·605
30	·423	·430
40	·313	·320
50	·241	·247
60	·191	·195
70	·155	·158
80	·129	·130
90	·109	·109
20-per cent. NaCl Solution.		
0	·0267	·0267
10	197	197
20	154	153
30	124	123
40	102	102
50	87	86
60	74	74
70	65	65
80	57	57
90	51	51

solution of NaCl places it outside the class of simple mixtures considered in what precedes.

The result of this investigation may be summed up as follows:—

(1) No one of the three theoretical formulæ (1), (2), (3) represents the viscosity of a mixture with sufficient closeness.

(2) The empirical formula $\left(\frac{1}{\eta}\right)^m = v_1\left(\frac{1}{\eta_1}\right)^m + v_2\left(\frac{1}{\eta_2}\right)^m$ with a suitable value for m gives a satisfactory representation.

(3) It leads also to Slotte's formula for the variation of viscosity of a liquid with temperature.

19 [illegible]

XXX. *On the Law of Cailletet and Mathias and the Critical Density.* By SYDNEY YOUNG, *D.Sc., F.R.S., University College, Bristol*[*].

IN a very interesting paper (*Mém. de la Soc. Roy. des Sci. de Liége*, sér. 3, ii. 1899) M. E. Mathias discusses the law of the Rectilinear Diameter, discovered in 1886 by M. Cailletet and himself, and the law of the corresponding states of matter. The law of Cailletet and Mathias may be stated simply in this way:—The means of the densities of liquid and saturated vapour for any stable substance are a rectilinear function of the temperature.

It has been shown (Mathias, *Ann. de la Fac. des Sci. de Toulouse*, 1892; Young, Phil. Mag. Dec. 1892, p. 506) that if the generalizations of van der Waals regarding corresponding temperatures, pressures, and volumes are correct, the angular coefficient α [$D_t = D_0 + \alpha t$, where D_t and D_0 are the means of the densities at $t°$ and $0°$ respectively] of the diameters of different substances should be directly proportional to their critical densities, and inversely proportional to their absolute critical temperatures; or that for any substance

$$\alpha = \text{const.} \times \frac{D_c}{T_c};$$

---

[*] Read June 22, 1900.

thus

$$\frac{\alpha T_c}{D_c} = \text{const.} = a.$$

M. Mathias points out that in order to test the truth of the law of corresponding states, it is only necessary to ascertain whether a is really a constant. He then discusses the conditions necessary for the determination of a.

For a certain number of substances the critical temperature and the densities of liquid and saturated vapour from about the ordinary boiling-point to the critical point have been determined; and in these cases there is no difficulty. From the mean densities at a series of temperatures α is found, and D_c is then calculated from the formula

$$D_c = D_0 + \alpha(T_c - 273).$$

In the great majority of cases, however, the only density determinations that have been made are those of the liquid below the boiling-point. We may, however, calculate the densities of saturated vapour at these low temperatures if the vapour-pressures are known, on the assumption that the vapour-density is practically normal; and thus the mean densities of liquid and saturated vapour may be ascertained.

Now the law of Cailletet and Mathias has been found to hold good for a considerable number of substances from the boiling-point to the critical point; and M. Mathias, making the very natural assumption that the law may be relied upon at lower temperatures, calculates the value of α from the mean densities below the boiling-point. If the critical temperature is known, the critical density is then calculated as before; but for most substances the critical temperature has not been directly determined; and M. Mathias discusses the methods, notably that of Thorpe and Rücker, that have been suggested for calculating this constant.

M. Mathias shows that if, in Thorpe and Rücker's formula

$$T_c = \frac{T_2 d_1 - T_1 d_2}{A(d_1 - d_2)},$$

$A = 2$, then it follows that $a = 1$.

He further shows how, if $a = 1$, it would be possible to ascertain both the critical density and the critical temperature by a geometrical method. In most cases, however, A differs sensibly from 2 and a from unity, and the geometrical method is then inapplicable; neither can the critical temperature be calculated with sufficient accuracy by employing the value of A, 1·995, adopted by Thorpe and Rücker.

It occurred to me that A, though not quite the same for different substances, might possibly be related to the composition in some simple way; and I have therefore calculated its value (taking 0° and the boiling-point under normal pressure as the two temperatures) for the thirty compounds referred to in this paper; these constants are given in Table I. Unfortunately there does not seem to be a sufficiently marked connexion between the values of A and the composition to be of much practical use.

M. Mathias arrives at the conclusion—which, I think (except for a few special cases), is quite justified—that it is necessary to make a direct determination of the critical temperature.

M. Mathias then proceeds to the examination of experimental data derived from various sources. The critical temperature, the vapour-pressures, and the densities of liquid chlorine have been very carefully determined by Knietsch; and M. Mathias has calculated the densities of the saturated vapour below the boiling-point ($-33°\cdot6$), and finds that the constancy of both a and D_c are apparently extremely satisfactory; but the value of a (·7675) is very far from unity. The value of D_c is ·5782; but it may be pointed out that the ratio of this to the theoretical density at the critical temperature and pressure as observed by Knietsch is only 3·03, a very low number.

Among the other substances examined by M. Mathias is normal decane, for which the densities of liquid have been determined only at low temperatures. In this case the values of α, a, and D_c seem to be at variance with those obtained by myself for the lower normal paraffins, as will be seen from the table below:

	α.	a.	D_c.
Pentane	·000460	0·931	·2324
Hexane............	·000446	0·967	·2343
Heptane	·000440	1·013	·2344
Octane	·000440	1·075	·2330
Decane............	·000380	0·928	·2471

For the four lower paraffins α and D_c show very slight variations, whilst a rises considerably with increase of molecular weight, so that the values calculated for decane appear improbable.

In view of these apparently abnormal results it seemed advisable to undertake a careful examination of the whole of the data which I have obtained for thirty substances. In all cases except the alcohols the critical densities were calculated by the method of Cailletet and Mathias, the mean densities above the boiling-points only having been used except for one or two substances; and though the deviations from the formula $D_t = D_0 + \alpha t$ differ somewhat considerably, there did not appear to be any definite tendency to curvature except possibly in a few cases. I have, indeed, attributed these deviations to errors of experiment; and this view was strengthened by the fact that for normal pentane, with which very careful determinations were made from 0° to within 0°·05 of the critical temperature, the deviations were exceedingly small and well within the limits of experimental error.

As will be seen later, however, it turns out that in choosing normal pentane for this special investigation I happen to have hit on the one substance which does not show the slightest deviation from the law of Cailletet and Mathias.

Since the publication of M. Mathias's paper I have calculated the mean densities of all thirty substances at intervals of ten degrees between 0° and the boiling-point; and it became evident that for many of them the deviations increased rapidly below the boiling-point. Moreover, on plotting all the differences between the mean densities and those calculated from the formula $D_t = D_0 + \alpha t$ against the temperature, distinct curvature was noticeable in many cases. This will be seen from the curves (fig. 1) for hexamethylene, benzene, normal heptane, and propyl acetate.

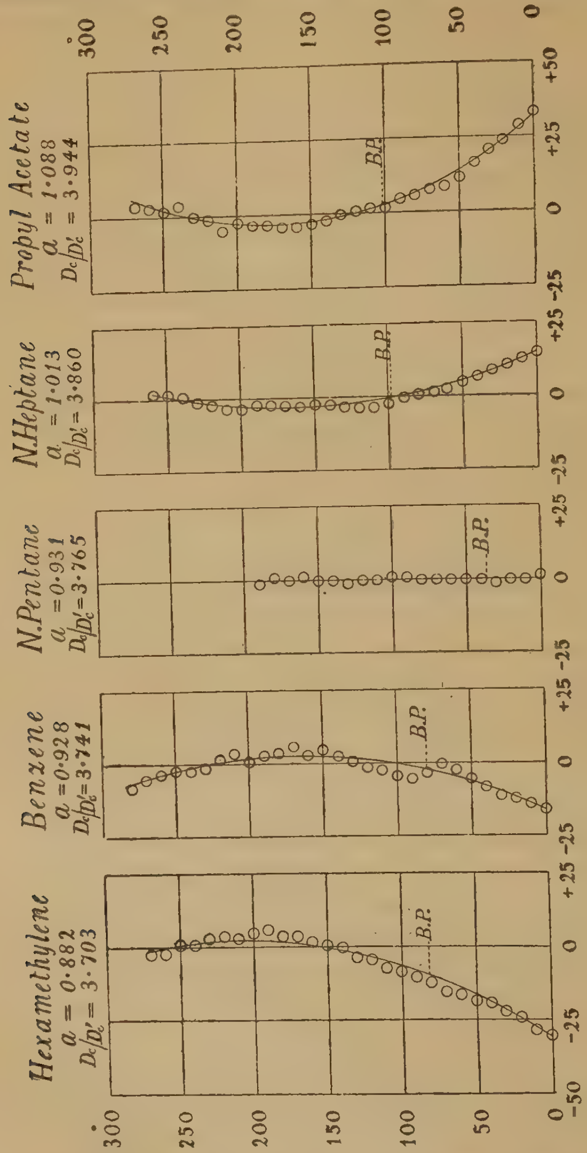
The drawn curves are calculated from the formula

$$D_t = D_0 + \alpha t + \beta t^2,$$

α being negative in these and all other cases (for both formulæ), whilst β is positive in the first two cases but negative in the last two.

For normal pentane it will be seen that there is absolutely no indication of curvature, so that $\beta=0$; for the alcohols, on the other hand, the curvature (in the same direction as that for propyl acetate) is so pronounced that a fourth term,

Fig. 1.



γt^3, has to be introduced into the formula to reproduce the data.

The values of a and of $\frac{D_c}{D'_c}$ [the ratio of the actual to the theoretical density at the critical point] are given for the five substances; those for methyl alcohol are very high, 1·142 and 4·521 respectively.

It is remarkable that as the curvature changes in such a manner that β passes from a positive value, through zero, to a negative value, a and $\frac{D_c}{D'_c}$ regularly increase. It is especially remarkable that for normal pentane, for which $\beta=0$, the value of $\frac{D_c}{D'_c}$ (3·765) is almost exactly that which may be taken as normal for substances whose molecules undergo no dissociation or polymerization. (The ratio given by van der Waals is $\frac{8}{3}=2\dot{\cdot}6$, but, as shown by Guye and by Heilborn, if we accept O. E. Meyer's correction for the relation between b in the formula of van der Waals and the space actually occupied by the molecules, this number should be multiplied by $\sqrt{2}$, which would give 3·77.)

That being so, we may perhaps take the normal value of a to be about 0·93.

It seems unnecessary to give the differences of the observed mean densities from those calculated from the formula $D_t=D_0+\alpha t$ at intervals of ten degrees for each of the thirty substances, but in Table I. I have given the values of D_0, $\alpha\times10^6$, a, $\frac{D_c}{D'_c}$, $\frac{D_c}{D'_c}-3{\cdot}770$, the difference between the observed and calculated mean density at 0°, and lastly A (Thorpe and Rücker).

The substances are arranged in ascending order of $\frac{D_c}{D'_c}$, and it will be noticed that there is, on the whole, a distinct tendency for a to rise; thus the values of a on the one side of normal pentane are, with one exception (stannic chloride), lower than ·931, and those on the other side are, again with one exception (fluorbenzene), higher.

Again, all the differences at 0° on the one side of normal pentane are negative, and with one exception (fluorbenzene) all on the other side are positive.

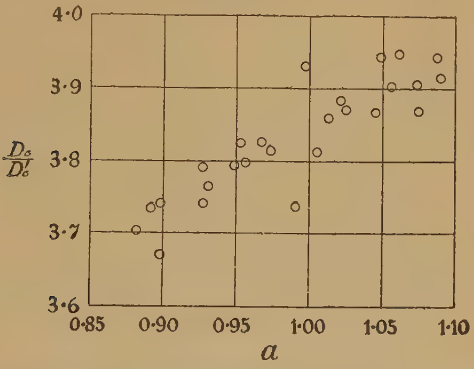
TABLE I.

Name.	D_0.	$a \times 10^6$.	$\alpha = a\frac{T_c}{D_c}$.	Error in Mean density at 0°. Calc.—Obs.	$\frac{D_c}{D'_c}$.	$\frac{D_c}{D'_c} - 3\cdot770$.	A (Thorpe and Rücker).
Carbon Tetrachloride	·8117	− 900	0·899	− 47	3·670	−0·100	1·996
Hexamethylene	·3954	− 436	0·882	− 30	3·703	−0·067	2·006
Isopentane	·3197	− 454	0·892	− 5	3·734	−0·036	1·984
Stannic Chloride	1·1356	−1240	0·991	− 38	3·738	−0·032	1·934
Benzene	·4485	− 502	0·928	− 16	3·741	−0·029	1·986
Di-isopropyl	·3395	− 433	0·899	− 4	3·741	−0·029	2·022
Normal Pentane	·3231	− 460	0·931	0	3·765	−0·005	1·994
Fluorbenzene	·5224	− 587	0·927	− 9	3·791	+0·021	2·030
Chlorobenzene	·5650	− 550	0·949	+ 11	3·794	+0·024	2·030
Iodobenzene	·9318	− 775	0·956	+ 15	3·798	+0·028	(2·030)
Di-isobutyl	·3567	− 433	1·005	+ 17	3·813	+0·043	1·978
Ether	·3687	− 547	0·974	+ 2	3·814	+0·044	1·937
Bromobenzene	·7634	− 694	0·953	+ 25	3·825	+0·055	(2·030)
Normal Hexane	·3390	− 446	0·967	+ 4	3·827	+0·057	1·982
Normal Heptane	·3518	− 440	1·013	+ 15	3·860	+0·090	1·980
Methyl Isobutyrate	·4577	− 583	1·045	+ 20	3·868	+0·098	1·956
Normal Octane	·3634	− 440	1·075	+ 42	3·870	+0·100	1·959
Propyl Formate	·4658	− 590	1·025	+ 14	3·871	+0·101	1·967
Ethyl Formate	·4759	− 649	1·021	+ 17	3·885	+0·115	1·959
Methyl Propionate	·4721	− 621	1·055	+ 27	3·903	+0·133	1·960
Methyl Butyrate	·4640	− 582	1·074	+ 39	3·907	+0·137	1·956
Ethyl Propionate	·4587	− 593	1·090	+ 25	3·917	+0·147	1·926
Methyl Formate	·5025	− 715	0·997	+ 6	3·932	+0·162	1·982
Propyl Acetate	·4585	− 587	1·088	+ 34	3·944	+0·174	1·943
Methyl Acetate	·4830	− 674	1·049	+ 32	3·945	+0·175	1·975
Ethyl Acetate	·4644	− 625	1·061	+ 22	3·949	+0·179	1·940
Ethyl Alcohol	·4138	− 556	1·043 *	+107	4·016 *	+0·246	2·280
Propyl Alcohol	·4184	− 528	1·030 *	+ 88	4·021 *	+0·251	2·277
Methyl Alcohol	·4190	− 602	1·142 *	+139	4·521 *	+0·751	2·255
Acetic Acid	·5399	− 587	0·994	+ 50	4·993	+1·223	2·077

from curve constructed graphically.

That there is a relationship of the values of a to the ratios $\frac{D_c}{D'_c}$ is clearly seen by the diagram (fig. 2).

Fig. 2.



With regard to the differences at 0°, M. Mathias notices (*loc. cit.* p. 19) that at low temperatures the substituted ammonias give values of α that increase as the temperature falls, but he regards this as being due to the approach to the solidifying-point.

It appeared to me more probable, however, that in most cases the mean densities would be more accurately represented by the equation

$$D_t = D_0 + \alpha t + \beta t^2$$

than by the simpler one $D_t = D_0 + \alpha t$, and I therefore calculated the constants D_0, α, and β for all the substances. For the alcohols, however, it was necessary to introduce a fourth term, γt^3, to get a satisfactory agreement.

I am indebted to Miss E. C. Fortey, B.Sc., for much valuable assistance with these calculations.

The constants are given in Table II., and here it will be seen that whilst the values of α are without exception negative, those of β on the one side of normal pentane are all positive, and, with three exceptions, those on the other side are negative. These exceptions are: fluorbenzene, which was before found to behave abnormally; hexane, for which $\beta = 0$; and methyl alcohol, for which γ has a very high negative value.

The relationship of β to $\frac{D_c}{D'_c}$ is well seen by the diagram (fig. 3).

Fig. 3.

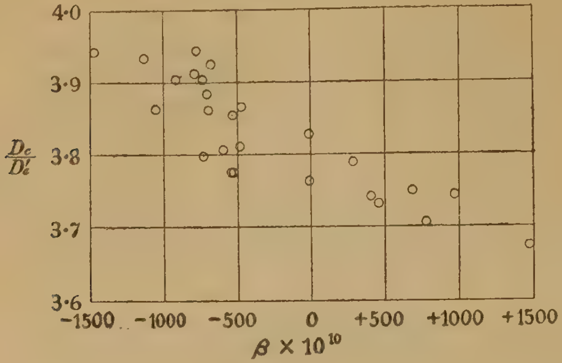


TABLE II.

Name.	D_0.	$\alpha \times 10^7$.	$\beta \times 10^{10}$.	$\gamma \times 10^{13}$.
Carbon Tetrachloride	·8165	− 9564	+1480	
Hexamethylene	·3985	− 4685	+ 791	
Isopentane	·3202	− 4658	+ 463	
Stannic Chloride	1·1387	−12760	+ 977	
Benzene	·4501	− 5248	+ 693	
Di-isopropyl	·3401	− 4445	+ 413	
Normal Pentane	·3232	− 4610	0	
Fluorbenzene	·5236	− 6000	+ 293	
Chlorobenzene	·5640	− 5337	− 509	
Iodobenzene	·9303	− 7556	− 519	
Di-isobutyl	·3550	− 4115	− 592	
Ether	·3685	− 5377	− 475	
Bromobenzene	·7609	− 6655	− 725	
Normal Hexane	·3388	− 4445	0	
Normal Heptane	·3504	− 4192	− 621	
Methyl Isobutyrate	·4558	− 5593	− 689	
Normal Octane	·3590	− 3954	−1046	
Propyl Formate	·4647	− 5748	− 459	
Ethyl Formate	·4741	− 6251	− 694	
Methyl Propionate	·4696	− 5921	− 729	
Methyl Butyrate	·4601	− 5430	− 906	
Ethyl Propionate	·4564	− 5644	− 784	
Methyl Formate	·5020	− 7013	− 665	
Propyl Acetate	·4553	− 5469	−1124	
Methyl Acetate...............	·4799	− 6280	−1467	
Ethyl Acetate	·4624	− 5992	− 764	
Ethyl Alcohol	·4028	− 3827	−5940	+ 651
Propyl Alcohol	·4095	− 3790	−3750	− 5533
Methyl Alcohol	·4050	− 4479	+1330	−23760
Acetic Acid	·5355	− 5366	−1191	

A comparison of the results by the two formulæ is given in Table III. Under $\frac{\Delta}{n}$ are given the mean differences multiplied by 10^4 between the observed and calculated densities without regard to sign; under $\frac{\Delta'}{n}$, the algebraical sum of the differences multiplied by 10^4 and divided by the number of observations.

The numbers under I. refer to the formula with two constants, those under II. to the formula with three constants (four for the alcohols).

Taking the whole range of temperature for each substance, it will be seen that the agreement when the three constants formula is used is very much better than when the simpler one is employed. Excluding the alcohols and acetic acid, the molecules of which are almost certainly of different complexity in the gaseous and liquid states, the mean value of $\frac{\Delta}{n}$ for the 26 substances is 5·40 for the formula with two constants as against 1·51 for that with three. That $\frac{\Delta'}{n}$ is very small in each case for the formula with three constants, not only for the whole range of temperature but also for the temperatures above and below the boiling-point taken separately, may be regarded as evidence that the curves represent the results with satisfactory accuracy; and, if that is so, the values of $\frac{\Delta}{n}$ for the same formula may be taken as a measure of the experimental errors which, it will be seen, differ considerably for different substances. The large errors in the case of stannic chloride may be explained by the fact that this compound attacks mercury at all temperatures whilst carbon tetrachloride does so at high temperatures, so that special experimental methods had to be devised. Again, the observations with iodobenzene had to be made by artificial light as the substance becomes rapidly coloured on exposure to daylight. Acetic acid gave a good deal of trouble at the highest temperatures, owing to repeated bursting of the tubes, but the comparatively large errors with ether and ethyl and propyl alcohol are not easily accounted for.

TABLE III.

Name.	$\frac{\Delta}{n}$.				$\frac{\Delta'}{n}$.					
	Whole Range.		Above B.-P.		Whole Range.		Below B.-P.		Above B.-P.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
Carbon Tetrachloride ...	12·00	2·54	4·15	3·05	− 8·57	−0·04	−31·62	−0·75	+ 0·65	+0·25
Hexamethylene...........	9·07	1·29	3·68	1·47	− 6·64	+0·07	−20·44	−0·67	− 0·07	+0·42
Isopentane	1·95	0·68	1·50	0·69	+ 0·26	−0·05	− 4·33	−0·67	+ 1·12	+0·06
Stannic Chloride	9·17	3·35	5·18	4·29	− 6·76	−0·17	−15·67	−0·33	− 0·47	−0·06
Benzene....................	4·69	1·34	3·25	1·50	− 2·48	+0·10	− 7·89	+0·56	− 0·05	−0·10
Di-isopropyl..............	2·57	1·09	2·06	1·06	− 0·30	−0·13	− 4·00	−0·05	+ 1·00	0
Normal Pentane	0·70	0·40	0·62	0·37	+ 0·10	+0·10	− 1·00	0	+ 0·37	+0·13
Fluorbenzene	4·72	2·24	2·21	2·10	− 1·48	+0·17	− 8·11	−0·78	+ 1·50	+0·60
Chlorobenzene	3·32	1·31	2·14	1·07	+ 0·39	−0·14	+ 1·93	−0·36	− 1·14	+0·07
Iodobenzene	4·29	2·50	2·55	3·56	+ 1·86	−0·14	+ 2·58	−0·74	+ 0·33	+1·11
Di-isobutyl	3·93	0·93	0·88	1·18	+ 3·21	−0·07	+ 8·64	+0·18	− 0·29	−0·24
Ether	3·90	3·45	4·56	4·06	− 1·30	−0·35	− 0·25	−1·00	− 1·56	−0·19
Bromobenzene	6·52	1·63	2·45	2·45	+ 4·89	+0·30	+ 9·31	+0·06	− 1·55	+0·64
Normal Hexane	1·25	1·21	1·24	1·06	+ 0·25	+0·04	+ 0·71	−0·71	+ 0·06	+0·35
Normal Heptane	3·81	0·74	2·18	0·82	+ 1·44	+0·15	+ 6·60	0	− 1·59	+0·24
Methyl Isobutyrate	4·78	1·78	2·24	2·29	+ 3·37	−0·07	+ 9·30	−0·50	− 0·12	+0·18
Normal Octane	10·83	1·00	2·29	1·29	+ 9·30	+0·20	+22·00	−0·46	− 0·41	+0·71
Propyl Formate	2·89	1·41	1·39	1·39	+ 1·56	−0·15	+ 5·89	+0·11	− 0·61	−0·28
Ethyl Formate............	5·46	1·08	3·06	1·11	+ 3·29	+0·08	+12·67	0	+ 0·17	+0·11
Methyl Propionate	7·12	1·69	3·28	1·62	+ 4·42	−0·15	+15·75	−0·62	− 0·61	+0·06
Methyl Butyrate	10·14	1·17	2·67	1·50	+ 8·55	+0·21	+22·36	−0·09	+ 0·11	+0·39
Ethyl Propionate.........	5·14	1·68	1·44	1·67	+ 3·64	−0·04	+11·40	−0·90	− 0·67	+0·44
Methyl Formate	2·00	1·36	1·78	1·55	+ 0·64	+0·27	+ 3·00	0	+ 0·11	+0·33
Propyl Acetate...........	7·54	1·04	2·53	1·00	+ 5·61	+0·04	+15·27	−0·36	− 0·65	+0·29
Methyl Acetate...........	7·62	1·42	3·00	1·67	+ 4·79	+0·25	+21·50	+0·67	− 0·78	+0·11
Ethyl Acetate	4·92	0·92	1·65	0·71	+ 4·12	+0·04	+11·87	−0·62	+ 0·59	+0·35
Ethyl Alcohol	29·40	4·28	14·59	5·18	+15·48	−0·52	+60·87	+1·25	− 5·88	−1·29
Propyl Alcohol...........	26·11	4·22	20·00	5·35	+ 5·30	−1·55	+33·70	+0·10	−11·29	−1·94
Methyl Alcohol	45·32	2·42	26·39	2·94	+15·88	+0·58	+94·00	+0·29	−14·50	+0·71
Acetic Acid	11·06	4·13	6·00	3·95	+ 4·63	−0·13	+19·33	−2·08	− 4·20	+1·15
Mean, excluding Alco- }	5·40	1·51	2·46	1·71	± 3·43	±0·14	±10·54	±0·43	± 0·64	±0·30

It remains to be seen whether the simpler formula $D_t = D_0 + \alpha t$ is sufficiently accurate to be employed for temperatures between the boiling-point and the critical-point. The values of $\frac{\Delta}{n}$ and $\frac{\Delta'}{n}$ above the boiling-point are therefore given in the table, and it will be seen that the improvement effected by introducing the third constant is very much smaller than for the whole range of temperature. Thus the mean value of $\frac{\Delta}{n}$ falls only from 2·46 to 1·71, as against 5·40 to 1·51 for the whole temperature range, and for $\frac{\Delta'}{n}$ the fall is only from 0·64 to 0·30 as against 3·43 to 0·14.

There is therefore for this range of temperature, except in the more extreme cases (near the top and bottom of the table), not very much to choose between the two formulæ.

On the other hand, a comparison of the values of $\frac{\Delta'}{n}$ for the two formulæ below the boiling-point brings out the difference between them in a most striking manner. For the formulæ with two constants the first eight values are negative, and the rest with one exception (ether, for which the experimental errors are large and the temperature range small) are positive, and, omitting the alcohols, they range from $-31·62$ to $+22·36$, or, including the alcohols, to $+94·00$. For the formula with three constants the + and − signs are fairly evenly distributed, and, excluding the alcohols and acetic acid, the extreme values are $-0·90$ and $+1·00$. Again, for the simpler formula, the mean value of $\frac{\Delta'}{n}$, excluding the alcohols and acetic acid, is $\pm 10·54$, but for the formula with three constants it is only $\pm 0·43$. It is quite clear from this that the constants for the formula $D_t = D_0 + \alpha t$ calculated exclusively from the densities at temperatures below the boiling-point would in many cases differ very considerably from those calculated from the densities at temperatures above the boiling-point; and that the differences between the calculated critical densities $\{D_c = D_0 + \alpha(T_c - 273)\}$ and also between the values of a in the two cases might also be considerable.

Thus for normal octane the numbers would be

	D_0.	a.	D_c.	a.
Below the boiling-point...	·3592	·000409	·2381	0·978
Above the boiling-point...	·3634	·000440	·2330	1·075

The constants calculated from the densities below the boiling-point approach fairly close to those obtained by M. Mathias for normal decane from the densities between 0° and 100° (p. 482) though, as might be expected from the higher molecular weight of decane and from the fact that the densities were not taken even to the boiling-point, the errors in that case are still greater.

There seems to be no doubt that, in order to find the critical density with the greatest possible accuracy, it would be best to make use of the whole of the available data and to employ the formula with three constants, thus

$$D_c = D_0 + a(T_c - 273) + \beta(T_c - 273)^2.$$

This has been done for the thirty substances, and the new and old critical densities, also the new values of $\frac{D_c}{D'_c}$, are given in Table IV.

For convenience of reference the critical temperatures and pressures, the specific gravities at 0°, and the boiling-points under normal pressure are also given in the table. The order is in ascending order of the recalculated values of $\frac{D_c}{D'_c}$.

It will be seen that the differences between the new and old critical densities are quite small. They are greatest for chlorobenzene, bromobenzene, and iodobenzene; but the critical temperatures of these compounds are very high, and the density determinations have only been taken to 260° or 270°. The greatest difference, that for iodobenzene, amounts to 0·55 per cent., and for this substance there is an extrapolation through 180°.

In the case of the alcohols the differences are not excessive because the old values were not obtained from the simple formula but graphically from curves drawn through the points representing the mean densities.

Of the remaining 26 substances benzene shows the greatest

TABLE IV.

Name.	Sp. Gr. at 0°.	B.-P. at 760 mm.	Critical Temperature.	Critical Pressure.	Critical Density.		$\frac{D_c}{D'_c}$.
					Old.	Corrected.	Corrected.
				millim.			
Carbon Tetrachloride	1·63255	76°·75	283°·15	34180	·5569	·5576	3·674
Hexamethylene	·79675	80·9	280·0	30250	·2733	·2735	3·706
Isopentane	·63930	27·95	187·8	25020	·2344	·2343	3·732
Di-isopropyl	·67948	58·1	227·4	23345	·2410	·2411	3·742
Stannic Chloride	2·27875	114·1	318·7	28080	·7404	·7419	3·744
Benzene	·90006	80·2	288·5	36395	·3037	·3045	3·750
Normal Pentane	·64539	36·3	197·2	25100	·2324	·2323	3·763
Iodobenzene	1·86059	188·45	448·0	(33910)	·5846	·5814	3·777
Chlorobenzene	1·12786	132·0	360·0	33910	·3670	·3654	3·777
Fluorbenzene	1·04653	85·2	286·55	33910	·3542	·3541	3·790
Bromobenzene	1·52182	156·0	397·0	(33910)	·4879	·4853	3·799
Di-isobutyl	·71021	109·2	276·8	18660	·2369	·2366	3·808
Ether	·73620	34·6	194·4	27060	·2624	·2622	3·811
Normal Hexane	·67696	68·95	234·8	22510	·2343	·2344	3·829
Normal Heptane	·70048	98·4	266·9	20415	·2344	·2341	3·855
Methyl Isobutyrate	·91131	92·3	267·55	25750	·3017	·3012	3·862
Normal Octane	·71848	125·8	296·2	18730	·2331	·2327	3·863
Propyl Formate	·92868	80·9	264·85	30440	·3095	·3093	3·868
Ethyl Formate	·94802	54·3	235·3	35590	·3232	·3232	3·885
Methyl Propionate	·93871	79·7	257·4	30030	·3123	·3124	3·904
Methyl Butyrate	·92006	102·75	281·25	26000	·3003	·3002	3·905
Ethyl Propionate	·91240	99·0	272·9	25210	·2969	·2965	3·912
Methyl Formate	1·00319	31·9	214·0	45030	·3494	·3489	3·926
Propyl Acetate	·91016	101·55	276·2	25210	·2964	·2957	3·934
Methyl Acetate	·95932	57·1	233·7	35180	·3255	·3252	3·942
Ethyl Acetate	·92436	77·15	250·1	28880	·3081	·3077	3·944
Propyl Alcohol	·81930	97·4	263·7	38120	·2752*	·2734	3·995
Ethyl Alcohol	·80625	78·3	243·1	47850	·2750*	·2755	4·024
Methyl Alcohol	·81020	64·9	240·0	59760	·2705*	·2722	4·549
Acetic Acid	1·06970	118·5	321·6	43400	·3511	·3506	4·986

* Critical density not calculated from formula $Dt = D_0 + at$, but read from curve constructed graphically.

difference, 0·26 per cent.; in fourteen cases it is less than 0·1 per cent.

The alterations in the order of the substances in the tables $\left(\text{depending on } \frac{D_c}{D'_c}\right)$ are few in number; di-isopropyl is brought next to isopentane; the four halogen derivatives of benzene are brought together, whereas in the old table bromobenzene was separated from the others; lastly, the new order of the alcohols is propyl, ethyl, methyl in place of ethyl, propyl, methyl.

In both tables the iso- and di-isocompounds have lower values of $\frac{D_c}{D'_c}$ than the corresponding normal compounds.

It is perhaps worth remarking that if, in the formula $a = \frac{\alpha T_c}{D_c}$, we take the value of α in the formula with three constants instead of in that with two, and if we exclude the alcohols and acetic acid, the variation in a is much smaller than before, the extreme values being ·916 and 1·039 as against ·882 and 1·090, and the change is especially marked in the case of the hydrocarbons, for which the new constants range from ·916 to ·968 as against ·882 to 1·075. Now α in the formula $D_t = D_0 + \alpha t + \beta t^2$ differs but little from what it would be in the formula $D_t = D_0 + \alpha t$ if we were to take only the densities below the boiling-point, and as the variation of a is smaller in this case, it is the more remarkable that this constant should be so very low (·7675) for chlorine.

In this respect chlorine resembles the alcohols ($a =$ ·717, ·746, and ·844), but the critical densities of the alcohols are abnormally high whilst that of chlorine appears to be very low. It would be of considerable interest if the densities of the saturated vapour of chlorine could be determined at high temperatures so that the values of α, a, and D_c could be ascertained with certainty, but the experimental difficulties would be very great.

GENERAL CONCLUSIONS.

1. The law of Cailletet and Mathias is very nearly, though in most cases not absolutely, true; it appears to be only

strictly true when the ratio of the actual to the theoretical density at the critical point $\left(\frac{D_c}{D'_c}\right)$ has the normal value 3·77.

2. The curvature of the "diameter" is generally smaller the nearer $\frac{D_c}{D'_c}$ approaches the normal value, and the nearer $a\left(=\alpha\frac{T_c}{D_c}\right)$ approaches the value 0·93.

3. The curvature is in nearly every case in opposite directions according as $\frac{D_c}{D'_c}$ is greater or less than 3·77, and as a is greater or less than 0·93, and is such that in the formula $D_t=D_0+\alpha t+\beta t^2$ β is positive when $\frac{D_c}{D'_c}$ is lower than 3·77 and negative when it is higher, α being negative in every case.

4. The curvature is generally so slight that the critical density may be calculated from the mean densities of liquid and saturated vapour at temperatures from about the boiling-point to within a few degrees of the critical point by means of the simpler formula $D_t=D_0+\alpha t$ with an error rarely exceeding 0·25 per cent. and generally not exceeding 0·1 per cent.

5. If, however, the critical density be calculated from the mean densities at low temperatures (say below the boiling-point) only, the error may be considerable; in the case of normal decane it is probably between 5 and 6 per cent.

6. As has been pointed out by M. Guye (*Archives des Sciences Phys. et Nat.* 1894, series 3, vol. xxxi.) the law does not, as a rule, hold good at all for substances the molecules of which differ in complexity in the gaseous and liquid states.

APPENDIX.

Since this paper was written Mr. K. Tsuruta has kindly sent me a copy of his 'Thermodynamic Notes,' No. 10 (Phys. Rev. 1900, x. p. 116) in which he discusses the "law of straight diameter" as applied to benzene. The conclusion he arrives at is that whilst the mean densities obey the law "in quite a satisfactory manner" not only from 80° to the critical-point, but also from 80° down to the triple point, yet a more minute examination showed the so-called diameter "to consist of two nearly straight parts meeting somewhere near the temperature

180° C., or, more strictly, to be a curve whose curvature is so slight that it can be so described."

This conclusion is practically in agreement with that stated in this paper.

DISCUSSION.

Mr. ROSE-INNES said that in his paper the author had used the generalizations of van der Waals, although the author himself had shown that they were not strictly true.

Dr. YOUNG said that the generalizations held accurately in some cases, although they did not in others. In all cases in which molecular association or dissociation did not occur they were approximately true, and it was advisable to study them in order, if possible, to ascertain the cause of the small deviations.

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XXXI. *On the Concentration at the Electrodes in a Solution, with special reference to the Liberation of Hydrogen by Electrolysis of a Mixture of Copper Sulphate and Sulphuric Acid. By* HENRY J. S. SAND, *Ph.D., Bowen Research Scholar at Mason University College, Birmingham*[*].

CONTENTS :—Historical introduction.—Theoretical consideration of the Liberation of Two Constituents at an Electrode.—Calculation of the Concentration in a Solution contained in a cylindrical vessel, across one end of which a constant flow of salt is taking place.—Application of results to obtain Values for the Concentration at the Electrode of the Solution of a single Salt and of a Mixture.—Experimental determination of the Time required till Hydrogen appears during Electrolysis of an Acid solution of Copper Sulphate.—A new method for determining the Diffusion-Coefficient of Copper Sulphate.—Experiments to show the great influence of Convection-Currents on the quantity of Hydrogen given off in the Electrolysis of an Acid Solution of Copper Sulphate.—Summary of results.

SINCE the electrolysis of mixtures first attracted the attention of scientists, three distinct views have been held about the processes which take place at the electrodes.

In 1857 Magnus[†] put forward the theory that in the solution of a mixture of two salts, only one is decomposed if a current of small density be employed ; if, however, the current-density exceeds a certain definite value, the second salt also suffers decomposition. He attempted to find this definite value in the case of a mixture of copper sulphate and sulphuric acid, ascribing it to a current-density which produced a visible amount of hydrogen at a vertical cathode within fifteen seconds. The result obtained was, that the value was roughly independent of size, distance, &c. of the electrodes, and only a function of the composition of the electrolyte.

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[*] Read October 26, 1900.

[†] Pogg. *Ann.* cii. p. 17.

About the same time Hittorf was engaged in his fundamental researches on the processes which take place within the electrolyte. His experiments, as is well known, proved that in the interior of the solution of a mixture of two salts, both take part in the conduction of the current at all current-densities. Regarding the process which takes place at the electrode, he at that time assumed that the ions of both salts were primarily deposited in the same proportion in which they had taken part in the conduction of the current within the liquid. In most cases, however, one of the components would act chemically upon the solution with a definite reaction-velocity; and it was only when this velocity was exceeded by the rate at which it was being primarily deposited at the electrode that its liberation would become perceptible *. Thus in a mixture of copper sulphate and sulphuric acid, hydrogen would be primarily liberated at all current-densities; but it would only become visible when the velocity with which it was supposed to decompose copper sulphate in the nascent state was exceeded by the rate at which it was being primarily set free.

It appears that it was Le Blanc who first insisted sufficiently on the fact that the mode of conduction of the current within any part of the interior of the electrolyte does not necessitate the same mode at the electrodes. His investigations having proved that the same minimum electromotive force must be applied to various acids and bases in order to cause the continuous passage of a current of appreciable magnitude through them, Le Blanc framed his well-known theory, that whereas

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* Pogg. *Ann.* ciii. p. 46.

conduction through the interior of an acid or a base is due in almost exclusive preponderance to its own ions, the transmission from the solution to the electrode must be ascribed primarily to the ions of water. Generalizing this statement, he expressed the view [*] that in a mixture of ions at an electrode those exclusively are set free which require the smallest E.M.F. for their liberation; and it is only when their concentration at the electrode has gone down to zero, that those requiring a higher E.M.F. for their liberation also appear. Thus in a mixture of copper sulphate and sulphuric acid, copper only should be deposited till its concentration at the electrode has gone down to zero, after which hydrogen also would be liberated.

The decomposition of mixtures has recently been examined theoretically by Nernst [†]. We shall consider the same subject from a slightly different point of view.

For this purpose we adopt the view, probably best adapted for the treatment of chemical problems, that the energy expended by the current in passing through the drop of potential at either electrode is the equivalent of the free energy required to effect the change from ionic to free state, or *vice versa*, taking place there, plus the energy expended on any other processes which may accompany the passage of the current, and which finally result in an irreversible heating-effect. For our purposes we are justified in considering each electrode separately, as we can always suppose the electrode not under consideration so large that the nature of the processes taking place there and the energy expended there per g.-ion do not vary appreciably with the current-strength. We shall suppose a mixture of two salts given, and consider the deposition of n_1 g.-equivalents of the cation most easily deposited. For the present we shall assume that if processes occur which irreversibly cause the production of heat, this quantity of heat shall be proportional to the number of g.-equivalents liberated, so that it can be represented by hn_1, h being a constant. Under these conditions, if w_1 be the quantity of free energy required to liberate one g.-equivalent, the amount of work done in the deposition of the n_1 g.-equivalents will be independent of the current-density and equal to $n_1(w_1+h)$. Now the quantity of electricity which causes this will, according to Faraday's law, have the value fn_1, f being Faraday's constant of $96540 \frac{\text{amp.} \times \text{sec.}}{\text{g.-equiv.}}$. Therefore, if the drop of potential from the electrode to the liquid be E, the work done by the current in passing through it will be $\mathrm{E}n_1f$, and this according to our assumptions is equal to $n_1(w_1+h)$, or $\mathrm{E}f=w_1+h$.

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[*] *Zeitschr. phys. Chem.* xiii. p. 172.

[†] *Zeitschr. phys. Chem.* xxii. p. 541.

This means that the difference of potential between the electrode and the liquid is independent of the current-density employed, and is always the same as the minimum E.M.F. necessary to deposit those ions which are most easily set free. If therefore there be ions of a second substance present, which require for their liberation a minimum E.M.F., $\mathrm{E}_2>\mathrm{E}$, none of them will be liberated so long as any of the ions first considered are left in contact with the electrode. It is only when $\mathrm{E}_2=\mathrm{E}$ that simultaneous deposition of both occurs. Our suppositions have thus proved equivalent to Le Blanc's view.

It should be noted that our assumption that any heating effect which may take place is proportional to the number of ions deposited, excludes the liberation of heat owing to anything in the nature of electrolytic resistance in the vicinity of the electrode, being bound up with the deposition of the ions—electrolytic heating in a given electrolyte being, as is well known, proportional to the square of the current. In arriving at our result, we also excluded the supposition that at high current-densities ions of the two salts should enter into chemical combination, forming complex ions.

As is well known, the E.M.F. necessary to deposit an ion from a solution on a given electrode varies within certain limits with its concentration in the solution. In the case of reversible processes it can be calculated in volts by Nernst's formula: $\mathrm{E}=0{\cdot}860\times10^{-4}\frac{1}{n}\mathrm{T}ln\frac{\mathrm{P}}{p}$, T being the absolute temperature, n the valency of the ion, p its osmotic pressure in the solution, and P its so-called solution-tension. When two monovalent metals of solution-tension P_1 and P_2 are being simultaneously deposited as a mechanical mixture, this equation in connexion with $E_1 = E_2$ leads to

$$0{\cdot}860\,Tln\,\frac{P_1}{p_1} = 0{\cdot}860\,Tln\,\frac{P_2}{p_2} \quad \text{or} \quad \frac{p_1}{p_2} = \frac{P_1}{P_2},$$

a formula which is given by Nernst in the paper quoted *.

* *Note.*—In his paper Nernst also gives a formula for the ratio γ of the quantity of the metal (1) deposited in g.-equivalents to the total number of equivalents liberated, the conditions being as above. This formula is based on the consideration which follows from the results just obtained, that if we have a solution containing the salts of two metals in a proportion in which they are not simultaneously deposited, the metal which is in excess of this proportion will at first be deposited alone until the proportion for simultaneous deposition be again attained. If we therefore start with a solution which contains the salts of two monovalent metals in the proportion given by the equation $\frac{p_1}{p_2} = \frac{P_1}{P_2}$, or, assuming complete dissociation and indicating concentrations by c,

$$\frac{c_1}{c_2} = \frac{P_1}{P_2}; \quad \ldots\ldots\ldots\ldots \quad (A)$$

then if we stir in such a manner as to keep the concentration uniform as nearly as possible, the ratio of concentrations which before stirring varied throughout the electrolyte, will have the tendency to become again uniformly

$$\frac{c_1'}{c_2'} = \frac{P_1}{P_2}. \quad \ldots\ldots\ldots\ldots \quad (B)$$

It is easy to see that from the two equations (A) and (B) the ratio γ mentioned above can be calculated to be $\gamma = \frac{P_1}{P_1 + P_2}$. This is the formula given without explanation by Nernst. It should, however, be particularly noted that this ratio γ is not the result of simultaneous, but of successive deposition of the two metals, depending on the rate of stirring, and that, as will be seen later (note, p. 513), the ratio of simultaneous deposition, *e. g.* at the beginning of the experiment, has a different value, irrespective of the fact whether the current employed be large or small.

In order to obtain formulæ referring to simultaneous deposition, when no stirring takes place we assume the electrolysis to take place in a cylindrical vessel bounded by its cathode, and indicate distances from it by x, times by t, and name the quantity of each ion crossing any section in the differential of time in the direction towards the electrode, *i. e.* from greater values of x to less, F_1dt and F_2dt respectively; then, assuming complete dissociation, we have for simultaneous deposition of the two (monovalent) metals as above,

$$c_1 = \frac{P_1}{P_2}c_2 \text{ for } x = 0;$$

According to Neumann *, when copper is deposited from the normal solution of its sulphate on a copper electrode, it produces an E.M.F. aiding the current of 0·515 volt; hydrogen, on the other hand, when it is reversibly deposited on a platinized platinum hydrogen electrode an E.M.F. of only 0·238 volt, *i. e.* a voltage higher by 0·277, is required to liberate hydrogen reversibly from a normal solution of its sulphate than is required to liberate copper under the same conditions.

Now according to Caspari's experiments †, a 0·23 volt higher electromotive force is required to set hydrogen free on a copper than on a platinized platinum electrode; *i. e.*, in order to deposit hydrogen on a copper electrode from a normal solution of sulphuric acid 0·507 volt more is required than to deposit copper on the same electrode from the normal solution of its sulphate. If we employ Nernst's formula to calculate the concentration of a copper solution, to deposit copper from which would require the same voltage as to liberate hydrogen from a normal solution of sulphuric acid at 15°, we find a value of about 2×10^{-18} normal. This means, according to the theoretical considerations advanced, that hydrogen will not be given off from an acid solution of copper sulphate till the concentration of the copper has practically gone down to zero at the electrode.

In apparent opposition to this, the experimental liberation of hydrogen from a not too concentrated acid solution of copper sulphate is a matter which can be accomplished by comparatively low current-densities, and doubt might well arise, whether the suppositions on which our deductions are

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from which follows:

$$\frac{\partial c_1}{\partial t} = \frac{P_1}{P_2} \frac{\partial c_2}{\partial t} \text{ for } x=0;$$

and as in every cross section $\frac{\partial F}{\partial x} = \frac{\partial c}{\partial t}$, this gives:—

$$\frac{\partial F_1}{\partial x} = \frac{P_1}{P_2} \frac{\partial F_2}{\partial x}, \text{ for } x=0.$$

(See also note on p. 513.)

* *Zeitschr. phys. Chem.* xiv. p. 222.

† *Ibid.* xxx. p. 93.

based were not at fault. It might be supposed that diffusion of the copper sulphate in the liquid would effectually hinder its concentration from going down to zero at the electrode with the rapidity which the experiments require in order to justify the theory. Indeed, as far as I can see, the idea that the concentration of the copper is zero at parts of an electrode from which hydrogen is being given off has not been entertained by any of the experimenters who have published work on a mixture of copper sulphate and sulphuric acid.

It must be remarked here that changes of concentration in a liquid are in most cases no doubt effaced to a much greater extent by convection-currents than by diffusion. But in order to test the theory, it is possible experimentally to do away with convection-currents almost entirely by the methods described in the experimental part; besides from its very nature convection must be an erratic phenomenon, not amenable to calculation and which could not be depended on, continuously and uniformly, to neutralize changes of concentration arising on the total surface of an electrode. In order to test the theory experimentally, it would be necessary to calculate the concentration of the copper ions at the electrode of an acid solution of copper sulphate from which copper alone was being deposited, under the supposition that only diffusion, and no convection, neutralized differences of concentration brought about by the current. Unfortunately neither the laws of conduction of the current nor those of diffusion in a mixture are completely known, and if they were, their application would probably involve extremely great mathematical difficulties. It is therefore not possible accurately to solve the problem just stated. As will be seen later on, we can, however, solve it within certain limits by first turning our attention to the following simpler case.

Problem: Let us suppose electrolysis to take place in a cylindrical vessel bounded at both ends by its electrodes. Let F g.-equivalents of salt be uniformly and constantly removed at one end, per unit of surface and time, and let the distance l from the electrode forming the other end be so great that changes of concentration occurring there do not affect the concentration at the electrode under consideration.

Further, let the initial concentration be uniform and equal to c_0 g.-equivalents per unit of volume. Find the concentration in the interior of the liquid and at the electrode at any given time t under the suppositions, that changes of concentration are neutralized by diffusion only, that this takes place according to Fick's law, and that it is not affected by the passage of the current through the liquid *.

As the concentration at any point of the liquid cannot be influenced by the nature of the cause producing the removal of the salt, it will be the same as that in a similar liquid in which a flow F was produced by a suitable gradient of concentration being artificially kept up immediately behind the electrode. In such a solution, and therefore also in the one under consideration, we have for the determination of the state of the liquid the first equation :

$$\mathrm{F} = \mathrm{K}\frac{\partial c}{\partial x}, \quad \text{for } x=0, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if concentrations at any point are indicated by c, distances from the electrode by x, and the diffusion-coefficient of the salt by K.

The uniformity of the concentration at the beginning of the experiment affords us the second equation :

$$c = c_0, \quad \text{between } x=0 \text{ and } x=l \text{ for } t=0, \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the general expression of Fick's law gives us the third :

$$\frac{\partial c}{\partial t} = \mathrm{K}\frac{\partial^2 c}{\partial x^2}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Equations 1 and 3 are satisfied by the following general solution :

$$c = \frac{\mathrm{F}}{\mathrm{K}}x + \sum_{n=0}^{n=\infty} a_n \cos\left(\frac{n\pi}{l}x\right)e^{-\frac{n^2\pi^2}{l^2}\mathrm{K}t}; \quad . \quad . \quad . \quad (4)$$

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* *Note.*—The equations given here as far as No. 5 have already been given by H. F. Weber in the elaboration of his beautifully conceived method for the determination of the diffusion-coefficient of $ZnSO_4$ (Wied. *Ann.* vii. p. 539). Concentrations in a solution subjected to alternating currents have been recently examined by Warburg (Wied. *Ann.* lxvii. p. 495).

and in order that equation 2 may be fulfilled, viz. that

$$c_0 - \frac{F}{K}x = \sum_{n=0}^{n=\infty} a_n \cos\left(\frac{n\pi}{l}x\right),$$

between $x=0$ and $x=l$,

we must, according to Fourier, make

$$\tfrac{1}{2}la_0 = \tfrac{1}{2}\int_0^l \left(c_0 - \frac{F}{K}x\right)dx = \tfrac{1}{2}lc_0 - \tfrac{1}{4}\frac{F}{K}l^2,$$

$$\tfrac{1}{2}la_n = \int_0^l \left(c_0 - \frac{F}{K}x\right)\cos\left(\frac{n\pi x}{l}\right)dx = -\frac{l^2F}{\pi^2n^2K}(\cos n\pi - 1),$$

which is equal to 0 or

$$\frac{2l^2F}{\pi^2n^2K}$$

according as n is even or odd.

Substituting these values in equation (4), we obtain

$$c = \frac{F}{K}x + c_0 - \tfrac{1}{2}\frac{F}{K}l + \frac{4lF}{\pi^2K}\left(\cos\pi\frac{x}{l}e^{-\frac{\pi^2}{l^2}Kt} + \frac{1}{9}\cos 3\pi\frac{x}{l}e^{-9\frac{\pi^2}{l^2}Kt} + \ldots\right)^{*} \quad (5)$$

or

$$c = \frac{F}{K}x + c_0 - \frac{4lF}{\pi^2K}\left(\tfrac{1}{8}\pi^2 - \cos\pi\frac{x}{l}e^{-\frac{\pi^2}{l^2}Kt} - \frac{1}{9}\cos 3\pi\frac{x}{l}e^{-9\frac{\pi^2}{l^2}Kt} - \ldots\right)$$

and remembering that :

$$\frac{\pi^2}{8} = \frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \ldots\ldots$$

we find

$$c = \frac{F}{K}x + c_0 - \frac{4F}{\pi K}\sum_{n=1}^{n=\infty}\frac{l}{\pi(2n-1)^2}\left[1 - \cos(2n-1)\pi\frac{x}{l}e^{-(2n-1)^2\frac{\pi^2}{l^2}Kt}\right].$$

The infinite series in the above expressions for c converge so slowly for large values of l, as to make them useless for numerical application. For $l=\infty$ all the single members of the series in the last equation become infinitely small, and

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[*] This equation also fulfils the condition $F = K\frac{\partial c}{\partial x}$ for $x=l$. It can therefore be taken accurately to represent the concentration in a cylinder of length l, filled *e.g.* with $CuSO_4$ into which F g.-equivalents are introduced per unit of surface and time at the anode and the same amount is being taken away at the cathode, a fact which is utilized by Weber.

the series assumes the nature of a definite integral. We shall convert it into a definite integral and make l infinite by the substitutions :

$$n=\frac{q}{dq},\quad \frac{l}{\pi}=\frac{\kappa}{dq},$$

dq being the differential of the variable q which assumes successively the values dq, $2dq\ldots\ldots q\ldots\ldots\infty$, and κ an arbitrary positive constant. We thus obtain :

$$c=\frac{F}{K}x+c_0-\frac{4F}{\pi K}\int_0^\infty dq\frac{\kappa}{4q^2}\left(1-\cos\left(\frac{2q}{\kappa}x\right)e^{-\frac{4q^2Kt}{\kappa^2}}\right).$$

The value of κ being arbitrary, we can make :

$$\frac{4Kt}{\kappa^2}=1,\qquad \text{i. e. } \kappa=2\sqrt{Kt},$$

and we find

$$c=\frac{F}{K}x+c_0-\frac{2F}{\pi K}\sqrt{Kt}\int_0^\infty\frac{dq}{q^2}\left(1-\cos\frac{xq}{\sqrt{Kt}}e^{-q^2}\right).$$

This expression is further simplified in the following manner: we differentiate twice according to x and obtain

$$\frac{\partial^2c}{\partial x^2}=-\frac{2F}{\pi K\sqrt{Kt}}\int_0^\infty dq\cos\frac{xq}{\sqrt{Kt}}e^{-q^2}.$$

The value of the integral occurring here being known to be $\frac{\sqrt{\pi}}{2}e^{-\frac{x^2}{4Kt}}$, we have :

$$\frac{\partial^2c}{\partial x^2}=-\frac{F}{K\sqrt{\pi Kt}}e^{-\frac{x^2}{4Kt}},$$

and making use successively of equations (3) and (2) we find

$$c=c_0-\frac{F}{\sqrt{\pi K}}\int_0^t\frac{dt}{\sqrt{t}}e^{-\frac{x^2}{4Kt}};\quad\ldots\ldots\quad(6)$$

an equation from which it is not difficult to obtain numerical values for c by one of the approximation methods. For the concentration at the electrode for which $x=0$, this equation assumes the extremely simple form

$$c=c_0-2F\sqrt{\frac{t}{\pi K}}=c_0-1{\cdot}1284F\sqrt{\frac{t}{K}}.\quad\ldots\quad(7)$$

Experimental application of equation (7).—(a) *Application to the Solution of a Single Salt.*

If we electrolyse the solution of a single salt, for example that of pure copper sulphate, we know that the value of F at the cathode in $\frac{\text{g.-equiv.}}{\text{cm.}^2\,\text{sec.}}$ is

$$\frac{in_a}{96540}=\frac{i(1-n_c)}{96540},$$

i being the current-density in $\frac{\text{amp.}}{\text{cm.}^2}$, n_a the transport value of the anion SO_4, and n_c that of the cation Cu in the solution. The concentration at the electrode after electrolysing for t seconds will therefore be

$$c=c_0-\frac{1\cdot 1284}{96540}\,in_a\sqrt{\frac{t}{K}}=c_0-\frac{1\cdot 1284}{96540}\,i(1-n_c)\sqrt{\frac{t}{K}}\,. \quad (8)$$

This formula can be employed for the determination of K if coordinate values of c and t are known. Before, however, further attempting to apply it to electrolysis, it will be necessary to consider to what extent the conditions on which it is based can be fulfilled in electrolytic experiments.

Let us suppose electrolysis of a pure copper-sulphate solution to take place in a cylindrical vessel of length l, bounded at the top by a horizontal cathode, at the bottom by a horizontal copper anode. In such a vessel, kept at constant temperature, convection-currents will be reduced to a minimum, as the lighter layers of less concentrated solution are continually being produced at the top, and the more concentrated ones at the bottom.

Our formula being based on the assumption of an infinitely distant anode does not comprise the fact that the anode of the real vessel we are now considering is causing a continuous flow of salt into the liquid at the distance l below the cathode, which is equal to the flow out of it. It is, however, not difficult to see that the following statements are correct:—(1) The real concentration at the anode and in the solution is greater than that given by the formula. (2) The difference between the real concentration and the calculated value is a maximum at the anode, and decreases continually as we approach the cathode. These first two statements can be inferred from the principle of superposition. (3) The real concentration at the distance $\frac{l}{2}$ below the cathode is (either according to Weber's formula (5) or from considerations of symmetry) constantly c_0; the difference between real and calculated values therefore is

$$\frac{F}{\sqrt{\pi K}}\int_0^t \frac{dt}{\sqrt{t}}\, e^{-\frac{l^2}{16Kt}}.$$

It is easy to see that as long as $t<\frac{l^2}{8K}$ the value of this function is smaller than

$$F\sqrt{\frac{t}{\pi K}}\, e^{-\frac{l^2}{16Kt}},$$

and from statement No. 2 we can conclude that the expression just given is also an upper limit for the difference between the real and calculated values at the cathode. In all the experiments carried out, this quantity is absolutely negligible.

We now come to the reconsideration of our assumption that diffusion in a solution is unaffected by the passage of a current through it. This question was first tested experimentally by H. F. Weber in the case of a zinc sulphate solution, and answered by him in the affirmative. It has recently been very thoroughly examined theoretically by Kohlrausch *. As shown by him, changes of concentration are in general brought about by the passage of a current through a solution of non-uniform concentration. These changes are in the case of a cylindrical vessel given for each ion in our notation by the formula

$$\frac{\partial c}{\partial t}=\pm\frac{i}{96540}\frac{\partial}{\partial x}\left(\frac{ac}{\kappa}\right), \quad . \quad . \quad . \quad . \quad (9)$$

in which c is the concentration of the ion under consideration, a is its mobility, and κ the conductivity of the solution. The positive or negative sign must be taken according as the ion is positive or negative (in contrast to Kohlrausch's notation, where the positive ions move from smaller values of

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* Wied. *Ann.* lxii. p. 209 (1897).

x to greater). As is known, $\frac{ac}{\kappa}=n$ is Hittorf's transport value of the ion under consideration, and we can write the above equation in the form

$$\frac{\partial c}{\partial t}=\pm\frac{i}{96540}\frac{\partial n}{\partial c}\frac{\partial c}{\partial x}, \quad . \quad . \quad . \quad . \quad (10)$$

from which it can be concluded that in the interior of a solution of a single salt in which the transport values are independent of concentration, no change of concentration is ever brought about by the passage of the current. In the case of copper sulphate, however, n_c, the transport value of the copper, is not independent of the concentration. It is given according to Kohlrausch by Hittorf and Kirmis as

$$\frac{\partial n_c}{\partial c}=-0{\cdot}047\frac{\text{cm.}^3}{\text{mg.-equiv.}}.$$

We have, therefore, for differences of concentration brought about by the passage of the current at every point of a copper-sulphate solution:

$$\frac{\partial c}{\partial t}=-\frac{0{\cdot}047}{96540}i\frac{\partial c}{\partial x}.$$

$\frac{\partial c}{\partial x}$ in our solutions being always positive, we can conclude that this effect will cause a general lowering of concentration, and that the value given by equation (8) for c is slightly too large and must be regarded as an upper limit.

We can also find a lower limit for c by the following considerations. The value of $\frac{\partial c}{\partial x}$ for $x=0$ is given by equation (1), we therefore know that at the electrode, owing to the effect we are considering alone

$$\frac{\partial c}{\partial t}=-\frac{0{\cdot}047\, i^2 n_a}{96540^2\text{K}},$$

$$\Delta c=-\frac{0{\cdot}047\, i^2 n_a}{96540^2\text{K}}t.$$

This value is, however, too large when taken to represent the total lowering of concentration. We see this when we remember that the gradient of concentration is always a maximum at the electrode, decreasing continuously as we depart from it, and that the lowering of concentration due only to passage of the current will therefore, according to the general equation (10), also be a maximum at the electrode, decreasing with increasing distance from it; this in its turn will have the effect of increasing the gradient at all points of the liquid and thus also increasing diffusion. We have therefore as extreme limits for the concentration at the electrodes of a copper-sulphate solution in which diffusion takes place according to Fick's law, the values given by the equation 8 and by the equation

$$c=c_0-\frac{1{\cdot}1284}{96540}\,i\,n_a\sqrt{\frac{t}{\mathrm{K}}}-\frac{0{\cdot}047n_a}{96540^2}\cdot\frac{i^2t}{\mathrm{K}}\quad . \quad . \quad (11)$$

It is of importance to know by how much the value of $\frac{i^2t}{\mathrm{K}}$ differs when determined by either the one or the other of these equations. This calculation does not offer sufficient interest to give it in detail, we shall therefore only state the result that the ratio of the difference between $\frac{i^2t}{\mathrm{K}}$ calculated by (11) or calculated by (8) is given sufficiently accurately by the expression

$$-\frac{2\times 0{\cdot}047}{1{\cdot}1284^2}\,\frac{c_0-c}{n_a};$$

which for values of

$$c_0=0{\cdot}2096\,\frac{\text{mg.-equiv.}}{\text{cm.}^3},\quad \text{and } c=0,$$

the only ones employed in the experiments, amounts to about 2½ per cent., *i.e.* K, calculated by (8), is 2½ per cent. smaller than calculated by (11).

In concluding these remarks it must be mentioned that, according to Wiedeburg's,[*] careful investigation of the diffusion of copper sulphate, this does not accurately follow Fick's law, the diffusion-coefficient decreasing slightly with increasing concentration. A thorough examination based upon Wiedeburg's law would, however, lead beyond the scope of this paper.

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[*] Wied. *Ann.* xli. p. 675.

(b) *Application of Equation* (7) *to a mixture of Copper Sulphate and Sulphuric Acid.*

As has already been stated, we shall in dealing with mixtures be obliged to confine ourselves to obtaining upper and lower limiting values for the concentration at the electrodes, which will enable us to follow the real values in broad lines in their dependence on initial concentration and current density. Great accuracy in these values will not be required, and we shall be justified in wholly neglecting influences which only slightly affect the results. We shall thus suppose, that in a mixture of copper sulphate and sulphuric acid, the diffusion of the former is not affected by the presence of the latter.

We first proceed to determine limits for the flow F, defined by F*dt* being the quantity of copper brought by diffusion in the differential of time to each unit of surface of the electrode, when copper alone is being deposited on it. Using the same notation as above, the flow of copper out of the solution at the electrode is

$$\frac{i}{96540}\,\frac{\text{g.-equiv.}}{\text{cm.}^2\,\text{sec}},$$

and the flow towards the latter, due to electrolysis

$$\frac{ac}{\kappa}\,\frac{i}{96540}\,\frac{\text{g.-equiv.}}{\text{cm.}^2\ \text{sec.}}.$$

The flow F due to diffusion is therefore

$$\frac{i}{96540}\left(1-\frac{ac}{\kappa}\right).$$

This quantity is variable, increasing continually from its original value to the value $\frac{i}{96540}$, which it assumes when c has gone down to 0. The quantity $\frac{ac}{\kappa}=n_c$, which we may call the transport value of the copper in the solution, can, as is known, be determined experimentally for the values of concentration and conductivity which exist at the beginning of the experiment. For this purpose it is necessary to pass an arbitrary quantity of electricity q through the solution, and to determine the decrease in copper in a region bounded on the one side by the anode, on the other by solution still having the original composition of the liquid (making the necessary correction for copper dissolved from the anode). This decrease is equal to $\frac{ac}{\kappa}\frac{q}{96540}$ g.-equiv., and has been determined by Schrader* in the case of certain mixtures—the same mixtures which have been employed for this present work. If the value of this decrease in grammes be α, and the quantity of silver deposited in a silver voltameter by the current employed be β, both of these values having been given by Schrader, then

$$\frac{ac}{\kappa}\frac{q}{96540}=\frac{\alpha}{31{\cdot}59}, \quad \frac{q}{96540}=\frac{\beta}{107{\cdot}66},$$

and

$$1-\frac{ac}{\kappa}=1-n_c=\frac{\frac{\beta}{107{\cdot}66}-\frac{\alpha}{31{\cdot}59}}{\frac{\beta}{107{\cdot}66}}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

the numbers 31·59 and 107·66 being the equivalent weights of copper and silver respectively.

We thus find that if we pass a current of constant density i through an acid solution of copper sulphate, until the concentration at the cathode has gone down to zero, the values of F at the beginning and at the end of the experiment can both be calculated, and we shall be justified in assuming that the concentration actually attained at any time t could also have been attained if a constant flow $F'=\frac{n'i}{96540}$ lying somewhere between the extreme values of F had taken place. Thus, as far as variability of F is concerned, we can express the concentration at the electrode at any time by the formula

$$c=c_0-\frac{1{\cdot}1284}{96540}n'i\sqrt{\frac{t}{K}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

n' being contained between 1 and the value of $1-n_c$ given in equation (12).

We now come to the consideration of the effect of the passage of the current through the liquid on its concentration. As has already been stated, this is expressed for a positive ion by the equation

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* *Ztschft. f. Elektrochemie,* iii. p. 502.

$$\frac{\partial c}{\partial t} = \frac{i}{96540} \frac{\partial}{\partial x}\left(\frac{ac}{\kappa}\right).$$

In the case we are now considering the concentration c of the copper will vary extremely rapidly as we approach the cathode, the conductivity κ of the solution on the other hand will remain fairly constant, as the solution, while becoming poorer in Cu and SO_4 ions, will at the same time become richer in H ions, which are brought to the electrode without being liberated there. As we only desire to obtain rough values, we shall therefore be justified in assuming κ constant and equal to the conductivity at the beginning of the experiment. The mobility of the copper we also assume constant. We thus have

$$\frac{\partial c}{\partial t} = \frac{ia}{96540\,\kappa} \frac{\partial c}{\partial x}.$$

As $\frac{\partial c}{\partial x}$ is always positive, we can conclude that the passage of the current will have the general effect of raising the concentration in parts of the liquid near and at the electrode where $\frac{\partial c}{\partial x}$ is of appreciable magnitude. The value given by equation (13) must therefore be regarded as a lower limit. Still more must

$$c > c_0 - \frac{1{\cdot}1284}{96540}\, i \sqrt{\frac{t}{K}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

We can also find an upper limit for c, by determining the increase of concentration Δc at the electrode due only to passage of the current through the solution, by a precisely similar method to that employed for finding the corresponding decrease in the case of pure $CuSO_4$ on page 508. In the way shown there, it can also be seen here that the value obtained is too large when taken to represent the combined effect of diffusion and passage of the current. As the final result, we obtain

$$c < c_0 - \frac{1\cdot1284}{96540} n'i \sqrt{\frac{t}{\mathrm{K}}} + \frac{an'}{96540^2\kappa} \frac{i^2}{\mathrm{K}} t\,^*;$$

$c_0 - c$ being always positive, this inequality can also be written

$$\epsilon(c_0 - c) = \frac{1\cdot1284\, n'}{96540} i \sqrt{\frac{t}{\mathrm{K}}} - \frac{an'}{96540^2\kappa} \frac{i^2 t}{\mathrm{K}},$$

where ϵ is a number smaller than 1. The values of $i\sqrt{\frac{t}{\mathrm{K}}}$

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* *Note.*—If we had made no assumption about a and κ this inequality would be

$$c < c_0 - \frac{1\cdot1284}{96540} n'i \sqrt{\frac{t}{\mathrm{K}}} + \int_0^t \frac{i}{96540} \frac{\partial}{\partial x} \left(\frac{ac}{\kappa}\right) dt,$$

from which, in conjunction with inequality No. 14, can be concluded

$$\frac{\partial c}{\partial t} = -\frac{1\cdot1284\, n'i}{2 \times 96540 \sqrt{\mathrm{K}t}} + \epsilon \frac{i}{96540} \frac{\partial}{\partial x} \left(\frac{ac}{\kappa}\right),$$

ϵ being a number contained between 0 and 1.

This formula enables us to obtain some further information about the ratio $\frac{\mathrm{F}_1}{\mathrm{F}_2}$, in which two monovalent metals can be deposited, which is mentioned in the note on p. 501, if we suppose that in the mixture assumed there the two salts diffuse independently of each other. The equation

$$\frac{\partial c_1}{\partial t} = \frac{\mathrm{P}_1}{\mathrm{P}_2} \frac{\partial c_2}{\partial t}$$

then leads to

$$\frac{\mathrm{P}_1}{\mathrm{P}_2} = \frac{-\frac{1\cdot1284\, n_1' i_1}{2 \times 96540 \sqrt{\mathrm{K}_1}} + \epsilon_1 \frac{i_1 \sqrt{t}}{96540} \frac{\partial}{\partial c} \left(\frac{a_1 c_1}{\kappa}\right) \frac{\partial c}{\partial x}}{-\frac{1\cdot1284\, n_2' i_2}{2 \times 96540 \sqrt{\mathrm{K}_2}} + \epsilon_2 \frac{i_2 \sqrt{t}}{96540} \frac{\partial}{\partial c} \left(\frac{a_2 c_2}{\kappa}\right) \frac{\partial c}{\partial x}},$$

from which for $t=0$ we obtain, remembering that for this value of t $n' = 1 - n_c$; and also that $\frac{i_1}{i_2} = \frac{\mathrm{F}_1}{\mathrm{F}_2}$:

$$\frac{\mathrm{F}_1}{\mathrm{F}_2} = \frac{\mathrm{P}_1(1 - n_{c_2})}{\mathrm{P}_2(1 - n_{c_1})} \sqrt{\frac{\mathrm{K}_1}{\mathrm{K}_2}}.$$

This equation for the limiting value of the ratio in which the two metals separate out in the first differential of time is based on no other assumption than that the two salts diffuse independently of each other, according to Fick's law (besides those assumptions stated on p. 498).

obtained from this quadratic equation are

$$10^{-4}i\sqrt{\frac{t}{\mathrm{K}}} = 5{\cdot}447\,\frac{\kappa}{a} \pm \sqrt{\left(5{\cdot}447\,\frac{\kappa}{a}\right)^2 - 93{\cdot}20\,\frac{(c_0-c)\epsilon\kappa}{n'a}}\,.$$

Now as we know that for $t=0$, also $c_0-c=0$, we conclude that only the negative sign before the square root is applicable. Remembering also that $\frac{n'}{\epsilon}$ is always greater than the value $1-n_c$ of equation (12), we can transform this equation into the inequality

$$10^{-4}i\sqrt{\frac{t}{\mathrm{K}}} < 5{\cdot}447\,\frac{\kappa}{a} - \sqrt{\left(5{\cdot}447\frac{\kappa}{a}\right)^2 - 93{\cdot}20\,\frac{(c_0-c)\kappa}{(1-n_c)a}}\,; \quad (15)$$

the dimension of the number 5·447 occurring here is $\frac{\text{amp.}\times\text{sec.}}{\text{g.-equiv.}}$ or, which is the same thing, $\frac{\text{milliamp.}\times\text{sec.}}{\text{mg.-equiv.}}$, and the dimension of the number 93·20 is $\left(\frac{\text{milliamp.}\times\text{sec.}}{\text{mg.-equiv.}}\right)^2$.

In the following Table (I.) I have given the concentrations of the solutions examined experimentally in g.-equivalents per litre, or, which is the same thing, in $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$. They have been made to correspond to solutions examined by Schrader*. The concentrations given by him have a slightly different meaning to mine, as his indicate the number of g.-equivalents contained in the copper-sulphate crystals which were dissolved in one litre of pure water. The quantities α, β, and κ, given by Schrader, as well as the values for a taken from Kohlrausch's tables, which have been used, will also be found in the table. Under the headings "i^2t_0 max." and "i^2t_0 min." will be found the maximum and minimum values of i^2t_0, calculated from the expressions (15) and (14) respectively, t_0 being the time required for c to go down to zero. In the column marked "i^2t_0 acc. to (16)" I have given values of i^2t_0 derived from the formula

$$c = c_0 - \frac{1{\cdot}1284}{96540}(1-n_c)i\sqrt{\frac{t}{\mathrm{K}}}, \quad . \quad . \quad . \quad . \quad (16)$$

$1-n_c$ being found by equation (12). These values are intermediate between those in the other two columns and given merely for comparison with the experimental numbers.

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* *Zeitschr. f. Elektrochem.* iii. p. 502.

At the end of the table I have also given the concentration of the solution of pure copper sulphate examined, and the value of $\frac{\mathrm{K}}{i^2 t}$ derived for it from equation (8), n_a having been taken as 0·63 *.

Table I.

My No.	Schrader's No.	My solutions.		Schrader's solutions.		a in g.	β in g.
		Conc. of Cu in $\frac{\text{mg.-equiv.}}{\text{cc.}}$	Conc. of H_2SO_4 in $\frac{\text{mg.-equiv.}}{\text{cc.}}$	Conc. of Cu in $\frac{\text{mg.-equiv.}}{\text{cc.}}$	Conc. of H_2SO_4 in $\frac{\text{mg.-equiv.}}{\text{cc.}}$		
A.	4	0·1634	0·0881	0·1670	0·0926	0·1743	0·00828
B.	5	0·2407	0·1327	0·2490	0·1375	0·2057	0·00988
C.	2	0·06618	0·0275	0·06618	0·0275	0·0903	0·00360
D.	10	0·1483	0·1804	0·1483	0·1804	0·2501	0·00860
E.	...	0·2096	...	...	...	...	...

Table I. (*cont.*).

My No.	κ in $(\text{ohm}\times\text{cm.})^{-1}$.	a in $\frac{\text{cm}^2}{\text{ohm}\times\text{mg.-equiv.}}$	$i^2 t_0$ max. (in milamp., sec., cm.)	$i^2 t_0$ min. (in milamp., sec., cm.)	$i^2 t_0$ acc. to 16 (in milamp., sec., cm.)
A.	0·027	15×10^{-3}	1609	836	1246
B.	$362\times10690\times10^{-8}$.	15×10^{-3}	3330	1773	27·6
C.	$79{\cdot}5\times10690\times10^{-8}$.	$17+10^{-3}$	265	141·0	192·3
D.	$391\times10690\times10^{-8}$.	15×10^{-3}	1064	691·5	925
E.	......	$\frac{\mathrm{K}}{i^2 t_0}=10^{-9}\times1{\cdot}195$ (milamp., sec., cm.).			

Note.—The value of κ for solution A has not been given by Schrader. The number 0·027 is an approximate value, calculated from Kohlrausch's tables.

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* According to Kohlrausch's tables, its value at the concentration 0·2 $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$ is 0·643, and at the concentration 0·02 it is 0·62.

In the calculation of i^2t_0 Wiedeburg's value for the diffusion-coefficient of copper sulphate at 18°,

$$K_{18} = 44{\cdot}79 \times 10^{-7}(1-3{\cdot}467\ c)\ \frac{\text{cm.}^2}{\text{sec.}}$$

was employed. Here the concentration c is supposed given in $\frac{\text{g. CuSO}_4}{\text{cm.}^3}$; when it is given in $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$ the number 0·2761 must be taken instead of 3·467. The value of $\underline{\text{K}}$ for $c=0$ has been taken in calculating the numbers contained in the columns "i^2t_0 max." and "i^2t_0 acc. to (16)"; and the value of K for the initial concentration in calculating the number i^2t_0 min. From the quantities i^2t_0 given in the table, which are based upon the diffusion-coefficient of copper sulphate at 18°, we should find i^2t_0 at θ degrees by the formula

$$i^2t_\theta = i^2t_{18}[1+0{\cdot}026(\theta-18°)],$$

in which 0·026 is the temperature-coefficient of diffusion assumed by Wiedeburg.

Experimental Part.

Determination of Time required till Hydrogen appears in the Electrolysis of an acid solution of Copper Sulphate.

A first series of experiments was performed to ascertain the time required till hydrogen first began to appear on electrolysing the mixtures of copper sulphate and sulphuric acid arranged in the preceding table, the solutions electrolysed being contained in cylindrical vessels, bounded at the top by horizontal cathodes. The values obtained are compared with the limits calculated by the formulæ given in the preceding table. Had hydrogen ever appeared before the lowest limit of time was reached, this would have proved conclusively that it was given off before the concentration of the copper at the electrode had gone down to zero. The upper limit could not be exceeded unless there were some considerable error in the experimental numbers employed.

Preliminary experiments were first carried out to study the subject qualitatively. It was found that on electrolysing the solutions with low current densities, horizontal cathodes being employed, which could be lit up for observation, at first only copper was deposited, after a certain time, however, varying greatly with the current density, the total surface of the electrode would suddenly within about half a minute become uniformly covered with tiny bubbles of hydrogen. The current was at the same time observed, the measuring instrument, as described later on, being either a Weston millivoltmeter or an Ayrton-Mather D'Arsonval galvanometer. When employing the former, the current seemed to remain absolutely constant till shortly before the hydrogen bubbles were visible, when suddenly a considerable drop would take place. In the actual quantitative experiments in which the Weston instrument was employed, the time which passed from the beginning of the experiments till this drop of the current occurred was taken as the time which elapsed until the hydrogen came off.

When employing the D'Arsonval, however, it was seen that the current at first kept slowly decreasing, until it would after a certain time drop considerably and then become fairly constant again. It was seen that after the drop had taken place, the hydrogen bubbles always began to appear. In the experiments in which the D'Arsonval was employed, the time when the sudden drop was completed was taken as that when hydrogen bubbles first appeared. In these experiments a Thomson-Varley rheostat was always introduced into the circuit, by regulating which the current was kept perfectly constant until the large drop occurred. The behaviour of the Weston instrument was probably due to a slight sticking effect.

Three types of apparatus were employed, which will be understood from the accompanying figures 1–3. Tubes of the first type were employed for experimenting on solution A. The cathode consisted of an engravers' plate. It was fixed to the end of the tube, which was ground perfectly flat, by Chatterton cement. As it allowed a spirit-level to be placed on its top, the apparatus could be adjusted so as to make the cathode perfectly horizontal. The anode in this apparatus consisted of copper gauze. As seen from the figure, the tube was closed by a rubber stopper, into which a groove *g* was cut to allow air-bubbles to be easily removed. The rubber tube *r* was filled by introducing a long thin glass tube into it, down which the solution was poured by means of a funnel. In the first few experiments tabulated, the original surface of the plate was employed. In the later experiments it was amalgamated in order to secure as uniform a deposit as possible. Apparatus of this type, of which several were made, showed the disadvantage, that the plate forming the cathode occasionally came off, besides it could not be readily removed for examination and cleaning purposes.

Fig. 1.

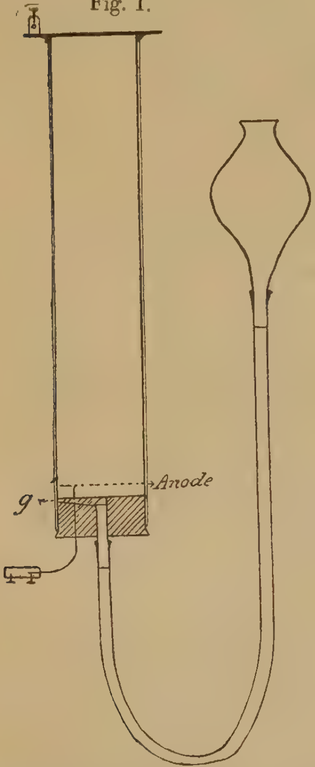
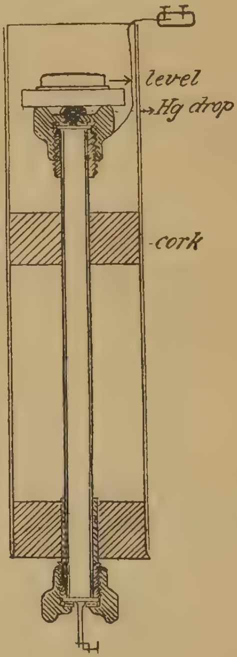


Fig. 2.

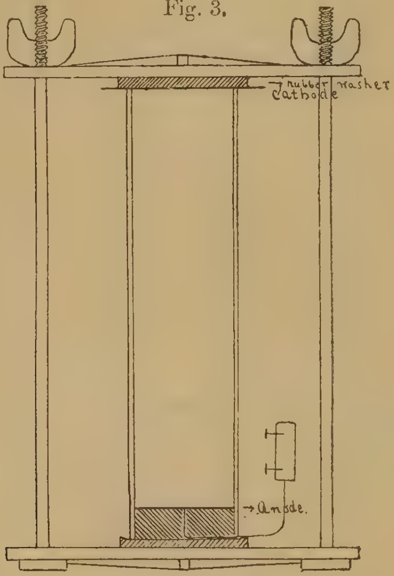


All the experiments on solutions B, C, D, and part of those on E were carried out in apparatus 2. It consisted of a polarimeter-tube. The top being originally bevelled had to be ground perfectly flat. The cathode consisted of a copper plate which was made perfectly flat, then polished and finally amalgamated. This was done by cleaning it with nascent electrolytic hydrogen, after which it amalgamated extremely readily, on dipping it into mercury. It was then again polished on perfectly clean chamois-leather, excess of mercury being removed from the edges by a pipette, drawn out to a fine point. This process of cleaning and polishing was repeated after each experiment. In order to avoid any liquid coming between the cathode and the surface of the glass forming the end of the tube by capillary action, this was greased with a trace of vaseline, so much only as could not be removed by a piece of dry filter-paper. The cathode was always fixed on the apparatus before introducing the liquid, by placing it in the cap, into which it fitted accurately, and then screwing down the glass tube on it. By always proceeding in this manner, all risk was avoided of any vaseline being spread on the surface of the electrode. The method of obtaining metallic contact through the cap by means of a drop of mercury will be understood from the figure. On the top of the cap a piece of plate glass was laid and on this a small spirit-level, it having been previously ascertained that it was possible to level the end of the polarimeter-tube by this means. The rest of the apparatus will be sufficiently understood from the figure. As seen, it was jacketed with water. The surface of the cathode was measured by accurately determining the length of the polarimeter-tube, and then weighing it out with mercury. It was found to be 0·699 sq. cm.

The apparatus 3 was only employed in the series of experiments on pure copper-sulphate solution, and only the last three values of Table VI. have been obtained with it. The cathode here again consisted of an engravers' plate, which reached beyond the surface of the tube and allowed a small level to be placed on its projecting part. In this apparatus the cathode could be easily observed, when suitably illuminated. Its surface was calculated as that of an ellipse from the length of two diameters of the tube, taken at right angles to each other with a screw-caliper. Its value was 3·782 sq. cm.

For the experiments the tubes were tightly clamped to a very heavy tripod stand of 1½ inch iron tubing, which was adjustable by three levelling-screws. As I was anxious to avoid vibrations, which are exceedingly great at Mason College, I followed a suggestion of Prof. Poynting's, and mounted the stand on three 50 kg. weights, each resting on three pieces of rubber. Before each experiment the tubes were allowed to rest for at least twelve hours.

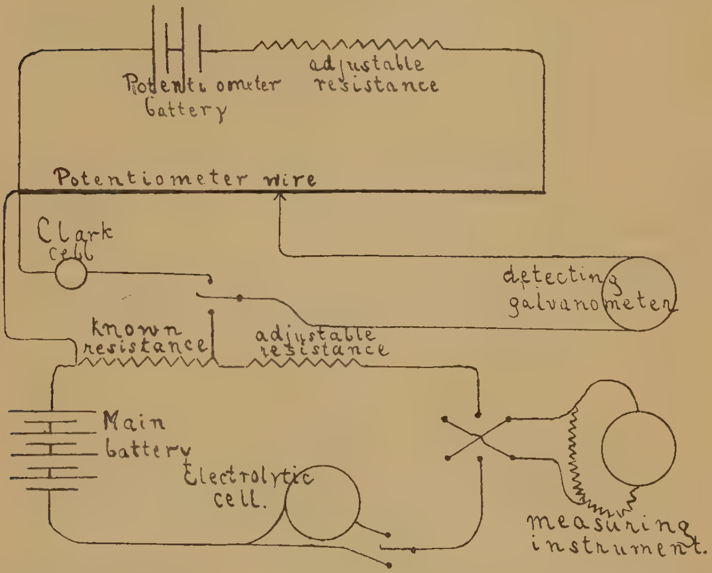
Fig. 3.



The solutions for electrolysis were prepared by diluting the requisite amount of carefully standardized copper sulphate and sulphuric-acid solution to 1 litre. The former solution, which was prepared from purest commercial copper sulphate, recrystallized twice, was analysed by electrolytic copper determination, the latter by precipitation with $BaCl_2$.

The electrical arrangements, which were in principle the same throughout all the experiments described, will be readily understood from the accompanying diagram (fig. 4). The current from a suitable number of accumulators was passed through a known resistance, an adjustable resistance, the electrolytic cell, and the measuring instrument, which, as already mentioned, consisted in all experiments either of an Ayrton-Mather D'Arsonval or a Weston millivoltmeter, in either case suitably shunted. The measuring instrument was carefully calibrated, and also standardized before each experiment by taking its reading when a current of approximately the same magnitude as that employed in the experiment was passed through it. This current was measured, as will

Fig. 4.



be sufficiently understood from the diagram, by determining the voltage on the ends of the known resistance by means of a separate potentiometer circuit.

As regards the degree of accuracy obtained in the experiments, the upper limit is probably reached by those arranged in Table V. The experiments here having all been repeated, this table shows the degree of coincidence which can be obtained in a series of determinations. The readings have in general been taken to within five seconds. The most serious errors are no doubt brought about by changes of temperature which cause convection-currents in the liquid. The accuracy of the experiments contained in Tables B and C, which were carried out in winter, has certainly been considerably reduced, owing to the heating arrangements of the building. Indeed, differences of as much as 10 per cent. have here in single cases been obtained in successive experiments which could not be accounted for in any other way. I have nevertheless not hesitated to give these earlier values as the ranges of the times obtained are so great that even differences of as much as 10 per cent. do not preclude a comparison with the theoretical values. These being calculated for 18°, should be multiplied by $1+0{\cdot}026\ (\theta-18)$ if the experimental values have been obtained at $\theta°$. I have instead made the corrections at the experimental numbers themselves, dividing them by $1+0{\cdot}026\ (\theta-18)$. It must be acknowledged that some uncertainty is introduced by this huge temperature correction. The temperature-coefficient for the diffusion of copper sulphate never having been experimentally determined has, as was also done by Wiedeburg, been assumed to be the same as that of other substances.

From the tables it will be seen that the experimental values are in all cases contained between the theoretical limits, and their differences from those calculated by the intermediate formula are in most cases not great. When we consider the extremely great ranges in which the times can be made to vary by varying the current-density, and also the numerous causes of experimental error, I think the medium formula No. 16 will be considered sufficient as an empirical expression of the results. From the fact that the values are always contained between the theoretical limits, and, besides, are far distant from the lower limit, I think we may conclude that these experiments prove within the limits which our theoretical knowledge of the processes taking place in the electrolyte allows, that liberation of hydrogen from an acid solution of copper sulphate takes place only after the concentration of the copper at the electrode has gone down to zero.

A New Method for the Determination of the Diffusion-Coefficient of Pure Copper Sulphate.

A second series of experiments was performed in order to study the behaviour of a pure copper-sulphate solution after the concentration of the copper at the electrode had gone down to zero.

After this is the case, diffusion can no longer bring sufficient

TABLE II.

Solution A, see Table I. Experiments in Apparatus 1.

Experimental Values.							Theoretical Values.		
No.	Current in milli-amps.	Surface of electrode in sq. cm.	Current-density in $\frac{\text{milliamps.}}{\text{cm.}^2}$	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	t acc. to eq. 16. $t=\frac{1246}{i^2}$	t minimum. $t=\frac{836}{i^2}$	t maximum. $t=\frac{1609}{i^2}$
1 ...	9·33	13·53	0·690	2480	16	2617	2618	1756	3380
2 ...	18·1	16·76	1·081	1010	14	1128	1068	717	1377
3 ...	20·5	13·53	1·515	510	17	524	543	364	701
4 ...	40·9	13·53	3·02	110	15	119	137	92	176
5 ...	51·6	13·53	3·88	75	13	86	85	57	107
6 ...	52·8	13·53	3·905	73	14	81	82	55	105
7 ...	57·4	13·53	4·24	62	15	67	69	47	90
8 ...	78·2	13·53	5·78	28	13	32	37	25	48

TABLE III.

Solution B, see Table I. Experiments in Apparatus 2.
Surface of Cathode ·699 sq. centim.

Experimental Values.						Theoretical Values.		
No.	Current in milliamps.	Current-density in $\frac{\text{milliamps.}}{\text{cm.}^2}$	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	t acc. to eq. 16. $t=\frac{2716}{i^2}$	t minimum. $t=\frac{1773}{i^2}$	t maximum. $t=\frac{3330}{i^2}$
1 ...	0·776	1·111	2025	12·4	2371	2201	1437	2698
2 ...	1·131	1·617	945	13·8	1060	1038	678	1274
3 ...	1·183	1·936	630	13·6	711	725	473	889
4 ...	2·09	2·99	290	13·8	318	304	199	372
5 ...	2·50	3·58	170	14·8	185	212	138	260
6 ...	2·617	3·74	165	13·6	186	195	127	238
7 ...	3·58	5·12	85	12·8	98	103	68	127
8 ...	5·10	7·30	40	13·8	45	51	33	62
9 ...	6·22	8·90	25	13·6	29	34	22	42

TABLE IV.

Solution C, see Table I. Experiments in Apparatus 2.
Surface of Cathode ·699 sq. centim.

Experimental Values.						Theoretical Values.		
No.	Current in milliamps.	Current-density in $\frac{\text{milliamps.}}{\text{cm.}^2}$	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	t acc. to eq. 16. $t = \frac{192 \cdot 3}{i^2}$	t minimum. $t = \frac{141 \cdot 0}{i^2}$	t maximum. $t = \frac{265}{i^2}$
1 ...	0·2123	0·304	1940	12·0	2299	2084	1528	2868
2 ..	0·2202	0·315	1960	13·0	2253	1938	1421	2671
3 ...	0·280	0·400	1040	12·8	1203	1202	881	1656
4 ...	0·406	0·581	550	13·6	621	570	418	785
5 ...	0·502	0·718	330	13·2	378	373	274	514
6 ...	0·768	1·099	150	14·2	166	159	117	219
7 ...	1·133	1·621	67	12·8	78	73	54	101
8 ...	1·801	2·576	23	13·8	26	29	21	40

TABLE V.

Solution D, see Table I. Experiments in Apparatus 2.
Surface of Cathode ·699 sq. centim.

Experimental Values.						Theoretical Values.		
No.	Current in milliamps.	Current-density in $\frac{\text{milliamps.}}{\text{cm.}^2}$	Time observed in seconds.	Temp. in ° C.	Time corrected to 18°.	t acc. to eq. 16. $t = \frac{925}{i^2}$	t minimum. $t = \frac{691 \cdot 5}{i^2}$	t maximum. $t = \frac{1064}{i^2}$
1 ...	0·402	0·575	2560	12·7	2970	2801	2094	3218
1 *a* ..	0·405	0·580	2600	12·7	3016	2753	2058	3163
2 ...	0·556	0·795	1355	12 5	1580	1463	1093	1684
2 *a* ..	0·557	0·797	1370	12·0	1604	1457	1089	1675
3 ...	0·734	1·051	750	12·0	888	839	627	963
3 *a* ..	0·737	1·054	750	12·0	888	833	622	958
4 ...	1·182	1·691	305	12·4	357	323	242	372
4 *a* ..	1·174	1·680	295	12·3	345	328	245	377
5 ...	1·847	2·64	120	12·4	140	133	99	153
5 *a* ..	1·885	2·70	120	13 0	138	127	96	146
6 ...	2·82	4·03	55	13·4	63	57	43	66

copper to the electrode to carry the current, for the formula shows that if the current were still conducted in the same manner as it was before, the concentration of the copper would become negative. It might therefore be supposed that it would be impossible to keep the current at its former strength. This is, however, found not to be the case.

In 1844 Smee* described an experiment, in which he electrolysed a solution of pure copper sulphate in a tall vessel, in the upper part of which he placed the cathode. His description of the varying appearance presented by the deposition of the copper as the concentration of his solution went down to zero runs:—"On the action of the galvanic force bright reguline copper first appeared at the negative pole, this was followed by a brittle, this by a sandy, this by a spongy deposit, this by black powder, and finally hydrogen was evolved." I have in general been able to verify Smee's observations as well as the fact, mentioned by him, that copper hydrate is formed at the electrode after the black powder has begun to appear. I have, however, in no case—neither when employing apparatus 3, nor when a form of apparatus was employed in which the solution was not contained in a closed vessel—been able to observe bubbles of hydrogen. It is therefore probable that Smee's copper-sulphate solution was more acid than mine. In my experiments the black spongy deposit always seemed to grow into the solution; in single cases it became intermingled with bright branches of metallic copper. The black deposit is evidently not pure copper, for it disappears when left for some time in dilute sulphuric acid. It is probably a copper hydride†.

The behaviour of the current while electrolysing a solution of pure copper sulphate was quite similar to that when an acid solution was examined. The black deposit always appeared after the large drop had taken place. The completion of the drop in the current was taken as the time when the concentration of the copper had gone down to zero. From a knowledge of this time and of the current-density employed, it is possible to calculate the diffusion-coefficient of copper sulphate by means of the expression given at the end of Table I. This has been done in Table VI.

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* Phil. Mag. xxv. p. 437.

† See Pogg. *Ann.* lxxv. p. 350.

Table VI.

Determination of Diffusion-coefficient K of copper sulphate. Solution E. Experiments 1–3 in apparatus 2; surface of cathode 0·699. Experiments 4–6 in apparatus 3; surface of cathode 3·782 sq. cm.

No.	Current in milli-amps.	Current-density in milliamps. / cm.^{2}	Time observed in seconds.	Temp. θ in °C.	K_θ by formula (Table I.) $K=10^{-9} \times 1{\cdot}195 i^2 t_0$ in cm.^{2}/sec.	K_{18}° by formula $K_{18}=\frac{K\theta}{1+0{\cdot}026(\theta-18)}$.	Mean value of K_{18}.
1 ...	·675	0·966	3390	14·4	$3{\cdot}79\times10^{-6}$	$4{\cdot}16\times10^{-6}$	$4{\cdot}46\times10^{-6}$
2 ...	1·004	1·436	1530	14·2	$3{\cdot}79\times10^{-6}$	$4{\cdot}21\times10^{-6}$	
3 ...	1·038	1·485	1515	13·8	$3{\cdot}99\times10^{-6}$	$4{\cdot}48\times10^{-6}$	
4 ...	6·68	1·766	1095	15·4	$4{\cdot}08\times10^{-6}$	$4{\cdot}38\times10^{-6}$	
5 ...	6·41	1·694	1285	15·0	$4{\cdot}41\times10^{-6}$	$4{\cdot}78\times10^{-6}$	
6 ...	6·37	1·683	1275	14·4	$4{\cdot}31\times10^{-6}$	$4{\cdot}76\times10^{-6}$	

According to Wiedeburg the diffusion-coefficient of copper sulphate at 18° is $4{\cdot}479\times10^{-6}\frac{\text{cm.}^2}{\text{sec.}}$ at the concentration 0, and $4{\cdot}220\times10^{-6}\ \frac{\text{cm.}^2}{\text{sec.}}$ at the concentration of solution E (see p. 516 & p. 509). Although the mean value for K_{18} in the above table is about what should be expected from Wiedeburg's determinations, yet the differences between the single experiments, none of which were known to have gone wrong in any respect, is too great to justify the recommendation of the method in its present form for more than a rough determination of diffusion-coefficients.

Experiments on the Effect of Convection-currents on the Relative Quantity of Hydrogen given off in the Electrolysis of an Acid Solution of Copper Sulphate.

The following experiments deal with the relative quantity of hydrogen produced by electrolysis of an acid copper-sulphate solution when considerably greater current-densities are employed than those used in the preceding experiments. This subject has been experimentally treated by Schrader in the paper already quoted, and by Houllevigne*.

Both investigators employed vertical electrodes and neither promoted nor hindered the natural convection-currents of their electrolyte. They found that their results were roughly expressed by hyperbolical functions.

From the results obtained in the foregoing part of this paper, the electrolytic evolution of hydrogen from an acid solution of copper sulphate is explained in the following manner. The concentration of the copper goes down to practically zero with great rapidity, as shown by the formulæ, when current-densities are employed which are considerably larger than those used in the preceding experiments. After this, diffusion no longer brings sufficient copper to the electrode to carry the current, and hydrogen is given off too in ever increasing quantity, until either the concentration of its ions has gone down to practically zero, or convection-currents bring new liquid to the electrode from which copper alone is again deposited. It will thus be seen that convection-currents play as great a part in the determination of the ratio of the two constituents as any of the other conditions of the experiment, and always have the effect of diminishing the relative quantity of hydrogen given off.

A lower limit of this quantity, when sufficient convection takes place, is thus always 0 per cent.; and the question might be asked, Is there an upper limit when we employ a given current-density, and use a large quantity of electrolyte; and what is its magnitude? I do not propose to discuss this question fully, but only to point out that, owing to the fact that convection-currents always have the tendency to diminish the production of hydrogen, such an upper limit can for all practical purposes be taken as represented by the relative quantity of hydrogen produced in a solution in which no convection-currents whatever interfere, at the time when the concentration of both copper and hydrogen ions at the cathode has gone down to practically zero. It is also possible to see from the formulæ given which are the main influences that determine this limit, by determining the lengths of time during which copper only and during which mainly hydrogen have been given off. They are, in the first place, the relative magnitudes of the expressions $\frac{c_0}{1-n_c}$ for the hydrogen and the copper ions, and, to a smaller degree, the relative values of the diffusion-coefficients of sulphuric acid and copper sulphate.

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* *Ann. Chim. et Phys.* [7] ii. p. 351 (1894).

I have discussed this question in view of some experiments that have been quite recently performed by Toepffer*, a short account of which will be found in the *Zeitschrift für physikalische Chemie*, xxx. p. 570. He deposited alloys of iron, cobalt, nickel, and zinc from mixtures of several of their salts, with the result that when his so-called low current-densities were employed, the metal requiring the higher E.M.F. for its liberation was always deposited in relative quantities which far exceeded its relative concentration in the solutions.

Firstly, as regards the values of the lowest current-densities used by the author, it seems probable that these would have been sufficient to make the concentrations at his cathode go down to zero in times varying from ten to one-tenth of a second if no convection-currents had interfered. This can be taken from the values given for concentrations and current-density in the thesis referred to, if, in order to obtain numerical values, we assume that diffusion-coefficients &c. had been the same in the author's solutions as in mine. None of his current-densities can therefore be described as small in the sense used in this paper; and I do not think there can be any doubt that if sufficiently small values had been used, the metal requiring the lower E.M.F. for its deposition would have preponderated in the alloy formed. As regards the actual preponderance of the baser of the two metals, a great deal of light could no doubt be thrown on this by determinations of transport values in the solutions examined, as will be seen from what has been stated above. If, as Toepffer assumes, the nobler metal has the tendency to form complex anions to a greater extent than the baser, this would certainly greatly influence the transport values in the direction required to explain the results.

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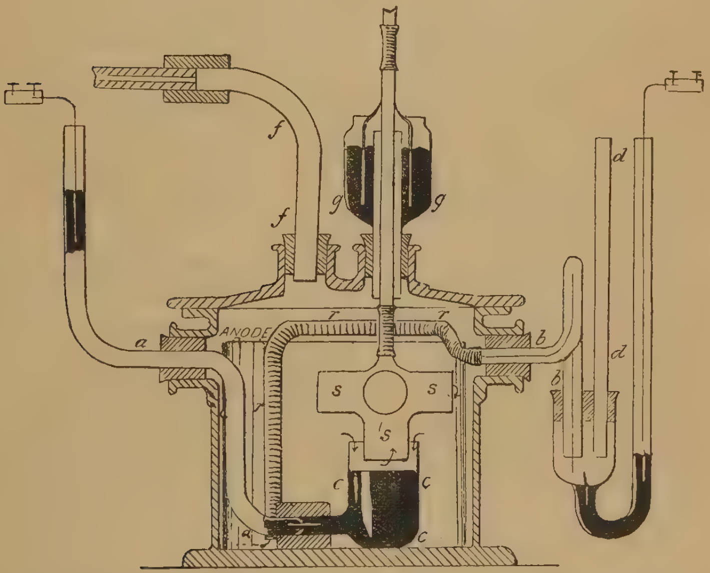
* Fully described in his thesis kindly sent me by the author.

The main purpose of the experiments I am now about to describe is to show to how great an extent the relative quantity of hydrogen, given off in the electrolysis of an acid solution of copper sulphate, is influenced by convection-currents; and also to show that when these are artificially increased by stirring, the hydrogen can be made to disappear altogether, even in cases in which otherwise more of its equivalents than of those of copper would have been liberated.

For this purpose the apparatus was devised, shown in the accompanying figure (fig. 5), which allowed the course of the electrolysis to be continually followed by measuring the quantity of hydrogen given off, and in which, at the same time, the solution above the cathode could, when desired, be rapidly renewed by vigorous stirring. It will be seen that it resembles a desiccator in general appearance, but has two openings in the side and two in the lid. Through one of the

Fig. 5.



side-openings the tube *a* passes leading to the cup *c*, which is filled with mercury, forming the cathode, uniform deposition of the copper being thus ensured. The glass tube *b* passing through the other side-opening is continued by the rubber tube *r*. It contains the wire leading to the anode, formed of a piece of pure electrotype copper, which lines the inside of the vessel. This tube also serves to pass hydrogen into the solution before each experiment. The tube *f* leads through the lid to the gas-burette. The gas-tight joint *g*, through which the stirrer passes, will be understood from the figure. It may be described as an inverted cup rotating in a ring of mercury. Glycerine is placed at the top of the mercury, and after the cup had become well moistened with the glycerine it could be made to rotate up to over 500 revolutions per minute without any considerable leakage occurring. When rotating at these very high velocities, a very slight escape of the hydrogen contained in the vessel took place; but this was in the nature of diffusion occurring through a porous cup, for it seemed independent of the pressure of the gas, and a correction could therefore easily be made for it. The stirrer *s* may be described as a modified Witt's stirrer. It has four hollow arms out of which the liquid is thrown by centrifugal force, being replaced by solution drawn from above the cathode. Owing to the great extent to which it causes the liquid in the vessel to rotate, which hinders the flow to the electrode, its efficiency decreases somewhat after it has been going for some time, and its velocity must be increased in order that the former efficiency may be obtained. The stirrer was fixed at its top to the end of the shaft from which it derived its motion by means of a short piece of rubber tube. It was also in connexion with a speed-counter.

In the experiments the apparatus was nearly filled with 600 c.c. of solution. Before use, a rapid current of hydrogen was passed through it for about half an hour by means of the tubes *d*, *b*, *r*, the gas escaping through a tap in the gas-burette. After this, mercury was poured down the tube *d*, which made a gas-tight joint and besides formed metallic contact for the wire leading to the anode. Either before or after each experiment, the apparatus was tested for leakage, the stirrer always rotating at about the same speed as it did in the experiment. The apparatus was mounted inside a large water-bath, to which also the pulleys &c. for the stirrer were fixed. It was made to order by Messrs. C. E. Müller & Co., of High Holborn, W.C.

The measuring-instrument for the current was in these experiments always the millivoltmeter mentioned above, the electrical arrangements being in principle exactly the same as those employed for the experiments described above.

The solutions employed are Nos. A and B of the previous experiments, which have also been examined by Schrader *; the minimum current-density employed by me being greater than the maximum value of 36 milliamperes per sq. cm. used by Schrader. Some results are given in the following tables. The quantities of hydrogen observed are corrected to 0° and 760 mm. The percentage ratio of the hydrogen given off to the total number of equivalents liberated has been calculated from the current employed. The time required for the concentration of the copper to go down to zero, calculated by means of the empirical equation 16, has been given in each case.

It will be seen from the results that when the solution is not artificially stirred, the quantity of hydrogen liberated decreases rapidly after the experiments have been going on for some time. This is evidently due to the rapid convection-currents brought about in the liquid by the electrolysis, and not to slight changes in the average concentration of the liquid, for when it was allowed to stand for about a day, the values found at the beginning of the experiment were again approximately attained. The experiments in which the solution was stirred were performed on different days to those in which no artificial stirring took place. It will be seen that in cases where otherwise over 60 per cent. of the equivalents given off would have consisted of hydrogen, the hydrogen could be made to disappear altogether. When a current-density was employed which would reduce the copper to zero in about 0·035 of a second, the stirrer could not make

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* Taken from his thesis kindly lent me by Prof. Warburg, in whose laboratory the experiments were carried out.

Table of Experiments on Influence of Convection.—Solution A. Surface of cathode 2·14 sq. cm.

No.	Current in amps.	Current-density in milliamps. / cm.^{2}	Time from beginning of minute	to	end of minute.	Average volume of hydrogen liberated per minute, corr. to 0° & 760 mm., in c.c.	Percentage ratio of equivalents of hydrogen to total equivalents liberated.	Time for concentration at electrode to become zero without convection by eq. 16, in seconds.	Revolutions of stirrer per minute.	Temp. of bath.
1.	0·120	56·1	1st	to	2nd	0·51	61 per cent.	0·4	0	12°
	,,	,,	3rd	,,	8th	0·37	44	,,	,,	,,
	,,	,,	9th	,,	12th	0·28	33	,,	,,	,,
	,,	,,	13th	,,	22nd	0·23	28	,,	,,	,,
	,,	,,	23rd	,,	28th	0·17	20	,,	,,	,,
1 *a.*	,,	,,	1st	,,	4th	0·00	0	,,	180	,,
2.	0·200	93·5	1st	,,	1st	0·64	46	0·14	0	12°
	,,	,,	2nd	,,	6th	0·51	37	,,	,,	,,
	,,	,,	7th	,,	11th	0·43	31	,,	,,	,,
	,,	,,	12th	,,	23rd	0·38	27	,,	,,	,,
	,,	,,	24th	,,	38th	0·37	26	,,	,,	,,
2 *a.*	,,	,,	1st	,,	3rd	0·06	4	,,	540	,,
3.	0·400	187	1st	,,	1st	1·44	51	0·035	0	13°
	,,	,,	2nd	,,	2nd	0·90	32	,,	,,	,,
	,,	,,	3rd	,,	5th	0·76	27	,,	,,	,,
	,,	,,	6th	,,	9th	0·48	17	,,	,,	,,
3 *a.*	,,	,,	1st	,,	1st	0·76	27	,,	325	,,
	,,	,,	2nd	,,	2nd	0·47	17	,,	,,	,,
	,,	,,	3rd	,,	4th	0·28	10	,,	,,	,,

Solution B.

No.	Current in amps.	Current-density in milliamps. / cm.^{2}	Time from beginning of minute	to	end of minute.	Average volume of hydrogen liberated per minute, corr. to 0° & 760 mm., in c.c.	Percentage ratio of equivalents of hydrogen to total equivalents liberated.	Time for concentration at electrode to become zero without convection by eq. 16, in seconds.	Revolutions of stirrer per minute.	Temp. of bath.
1.	0·120	56·1	1st	to	9th	0·52	62	0·56	0	13°
	,,	,,	10th	,,	11th	0·48	57	,,	,,	,,
	,,	,,	12th	,,	13th	0·43	51	,,	,,	,,
	,,	,,	14th	,,	17th	0·38	45	,,	,,	,,
	,,	,,	18th	,,	19th	0·31	37	,,	,,	,,
	,,	,,	20th	,,	30th	0·27	32	,,	,,	,,
1 *a.*	,,	,,	1st	,,	3rd	0·00	0	,,	290	12°

the hydrogen disappear altogether, but only decrease during the first minute to the extent to which it would have decreased if no stirring had been going on, owing to natural convection alone, after three minutes.

Summary of Results.

An equation (No. 8) has been derived and rigidly proved for calculating the concentration at the electrode of a solution of a single salt from which the metal is being deposited under the conditions that (1) the solution is contained in a cylindrical vessel bounded by the electrode ; (2) that no convection-currents occur ; and (3) that the diffusion of the salt obeys Fick's law and its transport values are constant. This formula can be made the basis of a method for roughly determining diffusion coefficients.

In the case of mixtures, it is possible to arrive at limits for the concentration; and it has been experimentally proved (1) that hydrogen always appears at the electrode of an acid solution of copper sulphate in which no currents of liquid are taking place, between the limits of time for the concentration to go down to zero ; and (2) that the time when it appears differs only slightly from that calculated by equation 16, which is the same in form as equation 8. It seems, therefore, that this formula can be taken as a sufficient empirical expression for the concentration at the electrode of a mixture too.

Lastly, the great part played by convection-currents in determining the ratio of the two constituents given off at the electrode of an acid copper-sulphate solution has been shown, it having been proved experimentally that by artificial stirring hydrogen can be made to disappear altogether in cases where it would otherwise have presented over 60 per cent. of the equivalents carrying the current from the solution to the electrode.

The experiments described here have been carried out entirely in the laboratories of Prof. P. F. Frankland and Dr. D. K. Morris, at Mason College, Birmingham, preliminary experiments having been performed in London at University College in the laboratories of Profs. Ramsay and

Callendar. I have pleasure in expressing my thanks to these gentlemen, as well as to Mr. A. W. Porter, of University College, London, for friendly interest shown in my work.

DISCUSSION.

Dr. LODGE, in summarizing the paper, said that no hydrogen was liberated until all the copper had gone, and that the formula for the concentration might be used again in further investigations.

Dr. DONNAN asked if the time at which hydrogen was liberated had been taken at the time at which hydrogen actually made its appearance in the form of bubbles, or whether any allowance had been made for saturation.

Dr. SAND said that in taking the completion of the increase of apparent resistance as the time at which hydrogen began to be given off, he had been guided simply by the empirical fact that bubbles of gas appeared shortly after this took place (10–40 seconds according to the current-density). He was unable to say whether local saturation and supersaturation perceptibly affected the increase of apparent resistance.

XXXII. *On the Refraction of Sound by Wind. By* EDWIN H. BARTON, *D.Sc., F.R.S.E., Senior Lecturer in Physics at University College, Nottingham*[*].

IN his treatise on Sound (vol. ii. pp. 132–4), Lord Rayleigh discusses the refraction of sound by wind where the rays are everywhere but slightly inclined to the wind, and obtains an approximate expression which, in the numerical illustration adduced, gives a result differing by only a few minutes of arc from the strict value. The theoretical interest of the wave propagation in this case seems, however, to warrant a slightly fuller examination of the problem on the basis of Huyghens' principle of wavelets and envelopes. Let us retain Lord Rayleigh's assumption as to the distribution of the wind, namely, that it is everywhere horizontal and does not vary in any one horizontal plane but is different at different levels.

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[*] Read November 9, 1900.

Then, confining our examination to rays in the same vertical plane as the wind, we find the following results :—

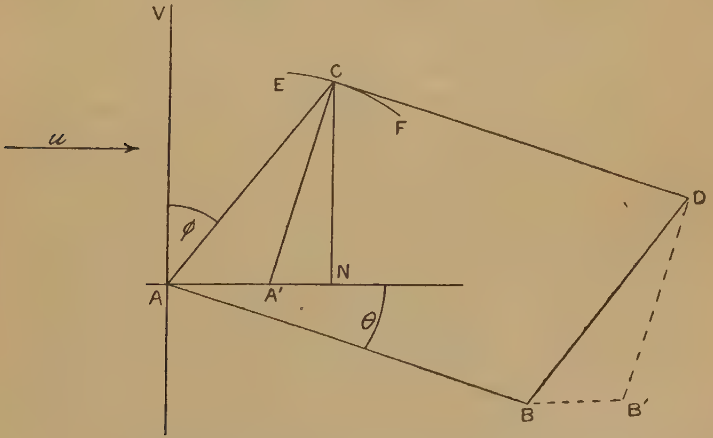
(1) The direction of propagation is not usually at right angles to the wave-front where there is a wind, consequently the cosecant law for the wave-front needs supplementing by another expression giving the direction of the ray.

(2) Total reflexion cannot occur if the wave-front is initially horizontal.

(3) In a region where the horizontal wind increases uniformly as we ascend, the rays instead of forming a catenary describe a more complicated curve which, however, reduces to a parabola in the special case of rays whose wave-fronts are horizontal.

Relation between Direction of Propagation and Wave-Front.—Let a region be imagined in all parts of which the wind is horizontal of speed u; let a plane wave-front be inclined θ to the horizontal, and let the direction of propagation of this wave of sound be inclined ϕ to the vertical. It is required to find ϕ in terms of θ, u, and v, the velocity of sound.

Fig. 1.—Drift of Sound-Rays in a Wind.



Let AB in fig. 1 represent the wave-front at a certain instant, and let CD represent it after the lapse of a short time denoted by t. Then the Huyghens' wavelet whose origin is A may be conceived as radiating from A in *every* direction at speed v compounded with the *horizontal* velocity u. Hence the wavelet from A after any time t is a circle whose radius is vt but whose centre is transferred a distance ut horizontally in the direction of the wind. Thus, lay off horizontally $AA'=ut$, then from A′ describe with radius vt the arc ECF, and we have the wavelet required. Similarly we get the wavelets originating at B and at any other points along AB. The new wave-front is the envelope CD of these wavelets, and is obviously parallel to AB. Also the direction of propagation of the wave is AC, making the angle $VAC=\phi$ with the vertical; whereas A′C is perpendicular to the wave-front which itself makes the angle $BAD=\theta$ with the horizontal. From C let fall CN perpendicular to the horizontal line AN. Then, for the relation between ϕ and θ, we have by construction

$$\tan NCA=\frac{NA}{CN}=\frac{NA'}{CN}+\frac{A'A}{CA' \cos NCA'}$$

or

$$\tan\phi=\tan\theta+\frac{u}{v}\sec\theta. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Accordingly the *ray*, instead of making the angle θ with the vertical as it would if normal to the wave-front, makes the angle ϕ, which usually differs from θ whenever there is a wind in the region in question. An exception occurs when θ is 90°, ϕ being then 90° also.

Refraction of Waves and Rays on crossing into a new Wind Zone.—Consider now two wind zones divided by a horizontal plane; let the wind in the lower zone be everywhere horizontal of speed u_0, and in the upper zone in the same direction but of speed u_1. Let a plane wave-front in the lower zone, inclined θ_0 to the horizontal, assume the inclination θ_1 after refraction into the upper zone. It is required to determine the relation between θ_1 and θ_0.

In fig. 2 let AC represent the wave-front incident at A upon the plane of separation AB of the two zones. Draw CB′ at right angles to AC, and lay off B′B, making $B'B : CB'=u_0 : v$. Then, by previous paragraph, CB is the direction of propagation in the lower zone. And, if t be the time occupied from C to B, we have $CB'=vt$ and $B'B=u_0t$. To construct the new wave-front in the upper zone it is necessary to consider A as the origin of a wavelet as in the first case. The wavelet is obviously a circular one of radius $A'Q=vt$

described about a centre A′, distant horizontally $u_1 t$ from A. From B draw BQ tangential to this arc, then BQ is the refracted wave-front required. And we have by the figure

$$\operatorname{cosec} QBA' = \frac{BA'}{A'Q} = \frac{B'A - AA' + B'B}{vt}$$

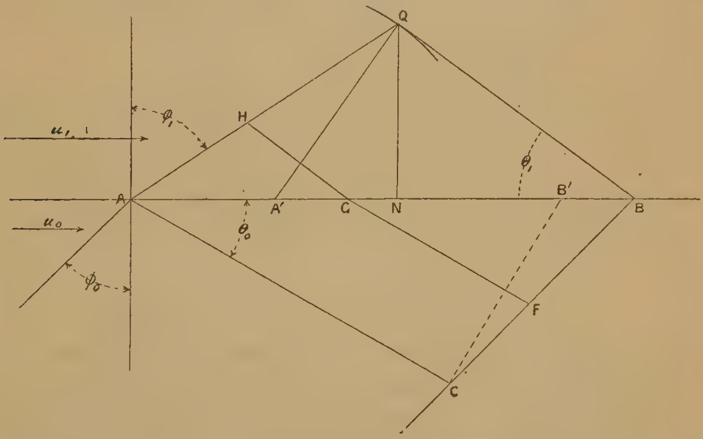
$$= \frac{B'A}{B'C} - \frac{u_1 t - u_0 t}{vt},$$

or

$$\operatorname{cosec} \theta_1 = \operatorname{cosec} \theta_0 - \frac{u_1 - u_0}{v}. \quad . \quad . \quad . \quad . \quad (2)$$

This result is obtained very simply by Lord Rayleigh by consideration of the velocity of the trace of the wave-front on the surface of separation, *i.e.*, referring to fig. 2, the velocity of the point G along AB. This velocity is seen to be susceptible of two expressions according as G is treated as a point on FG or as a point on GH. Rayleigh thus obtains

Fig. 2.—Refraction of Sound by abrupt change of Wind Speed.



$$\frac{v}{\sin \theta_0} + u_0 = \frac{v}{\sin \theta_1} + u_1, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is identical with (2) already found by Huyghens' principle. The advantage of the longer method adopted here lies in its power to treat the direction of propagation also. Thus, by equation (1), or by fig. 2, in which QN is perpendicular to AB, we have

$$\tan\phi_1 = \tan\theta_1 + \frac{u_1}{v}\sec\theta_1, \quad . \quad . \quad . \quad . \quad (4)$$

which completes the solution.

Refraction through any Number of Parallel Wind-Zones.—Consider, now, any number $(n+1)$ of horizontal zones, in each of which the wind is everywhere the same and horizontal, but let the wind-speeds in the different zones, beginning from the lowest, be u_0, u_1, u_2, . . . u_n, and let the angles which the wave-fronts make with the horizontal and the rays with the vertical be denoted respectively by θ and ϕ with corresponding subscripts. Then from (2) we have

$$\begin{aligned} \operatorname{cosec}\theta_1 &= \operatorname{cosec}\theta_0 - (u_1 - u_0)/v, \\ \operatorname{cosec}\theta_2 &= \operatorname{cosec}\theta_1 - (u_2 - u_1)/v, \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \operatorname{cosec}\theta_n &= \operatorname{cosec}\theta_{n-1} - (u_n - u_{n-1})/v. \end{aligned}$$

Hence, on addition, we obtain

$$\operatorname{cosec}\theta_n = \operatorname{cosec}\theta_0 - \frac{u_n - u_0}{v}. \quad . \quad . \quad . \quad (5)$$

Also by (1) or (4) we have for the final direction of propagation

$$\tan\phi_n = \tan\theta_n + \frac{u_n}{v}\sec\theta_n. \quad . \quad . \quad . \quad . \quad (6)$$

We thus see that the final inclination of wave-front and direction of propagation are each independent of the constants characterizing the intermediate zones. It should be noted, however, that a cosecant cannot have a value between $+1$ and -1, so that if any of the zones required this, the series must cease there, equations (5) and (6) not holding for higher zones. This brings us to the next topic.

Total Reflexion.—Although the cosecant law for the wave-front obtaining here differs from the ordinary optical law of refraction, we still have, as in optics, the phenomenon of total reflexion possible. And it is in this connexion that the distinction between wave-front and direction of propagation is most striking. Thus, for the wave-front, if the angle of refraction θ_n is put $\pi/2$, we have from equation (5) the critical case expressed by

$$\operatorname{cosec} \theta_0 - \frac{u_n - u_0}{v} = 1. \quad . \quad . \quad . \quad . \quad (7)$$

Hence any pair of values of θ_0 and $(u_n - u_0)$ which violates (7) affords an example of total reflexion, the last zone not being entered by the beam.

Suppose now that we have a series of wind-zones in which the wind-speed increases as we ascend: then, provided the *initial* inclination of the wave-front were *finite*, it is clear that at some point we must have total reflexion. But if, on the other hand, the wave-front were initially horizontal, we should then have $\theta_0 = 0$, and, by equation (5), all the θ's would be zero also. That is, we should have *no refraction* of the *wave-front*, and consequently *no total reflexion anywhere*, whereas the *ray*, as we ascend, *deviates without limit* from the vertical, for equation (6) now reduces to

$$\tan \phi_n = u_n/v. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

So that in this case we have *zero* refraction of the wave-front associated with *unlimited* refraction of the rays, *total reflexion being impossible.*

On consideration of the case by Huyghens' principle, it is seen that where a zone cannot be penetrated, and total reflexion occurs, the reflexion follows the ordinary optical law, angle of reflexion equals angle of incidence.

Path of Rays where Wind increases continuously with Height.—Let the wind be everywhere horizontal, and in the same vertical plane, but let its speed vary from one level to another according to the equation

$$u/v = c + ay, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where u is the speed of the wind, v that of sound, c and a are constants, and y is measured vertically upwards. The x coordinate will be taken horizontally to leeward. It is now required to determine the inclinations of the wave-front and of the rays at any point, *i. e.*, we require θ, ϕ, and x for any given y. The equations for θ and ϕ are derived immediately from (5), (6), and (9). Thus, dropping subscripts, we have

$$\left.\begin{array}{l} \operatorname{cosec} \theta = \operatorname{cosec} \theta_0 - ay \\ \text{or} \quad \operatorname{cosec} \theta = z = b - ay \end{array}\right\}, \quad . \quad . \quad . \quad (10)$$

where $z = \operatorname{cosec}\theta_0 - ay$, and $b = \operatorname{cosec}\theta_0$;

also
$$\tan\phi = \frac{dx}{dy} = \tan\theta + (c + ay)\sec\theta, \quad . \quad . \quad (11)$$

whence
$$x = \int \frac{dy}{\sqrt{z^2-1}} + \int \frac{(c+ay)z\,dy}{\sqrt{z^2-1}} \quad . \quad . \quad . \quad . \quad (12)$$

The first integral here represents the catenary found by Lord Rayleigh for the path of the ray when taken at right angles to the wave-front. The second integral is a small correction for the obliquity of the ray, and arises from the second term on the right side of equation (6). On evaluation (12) yields

$$2ax = (b+2c)\sqrt{b^2-1} - (b+2c+ay)\sqrt{z^2-1} + \log_e \frac{b+\sqrt{b^2-1}}{z+\sqrt{z^2-1}}. \quad (13)$$

Thus, for any given ordinate, the abscissa is the sum of three terms, the first being a constant, the second forming with y a curve of the fourth degree, while the third is the abscissa of a catenary. This is the general expression exhibiting the relation between x and y, and therefore completes the required solution. In considering various special cases it will, however, often be simpler to go back to equations (10) and (11).

Ray with Horizontal Wave-Front.—We now have $\theta_0 = 0$, $b = \operatorname{cosec}\theta_0 = \infty$, and (13) becomes indeterminate; so, either by evaluating it or by use of (10) and (11), we obtain

$$2x = 2cy + ay^2, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

i. e., the path of the ray is the parabola

$$\left(y + \frac{c}{a}\right)^2 = \frac{2}{a}\left(x + \frac{c^2}{2a}\right). \quad . \quad . \quad . \quad . \quad (15)$$

If the ray starts in still air, put $c = 0$, and we obtain

$$y^2 = 2x/a, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

a parabola with vertex at the origin.

Numerical Illustrations.—To exhibit the two phenomena of total reflexion and the parabolic path of rays with total reflexion impossible, take the following numerical data. Let the region be specified by equation (9), where $c = 0{\cdot}02$

and $a = 0{\cdot}0001$, *i. e.*,

$$\frac{\text{speed of wind}}{\text{speed of sound}} = {\cdot}02 + {\cdot}0001y, \quad . \quad . \quad . \quad (17)$$

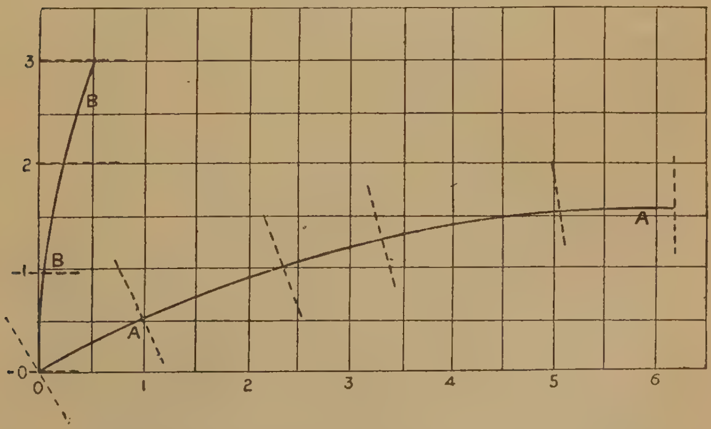
y being expressed in feet. Then, if the temperature is such as to make the speed of sound 1100 feet/second, the wind-speed at the origin is 22 ft./sec., = 15 miles per hour. Whereas at 1000 feet high the speed of the wind would be 90 miles per hour. In this region let sound at the origin of coordinates start down-wind and in the same vertical plane, and with

(1) its wave-front initially inclined at 60° to the horizontal. Then it suffers total reflexion at a point about 1547 feet higher than the origin, and at a horizontal distance of about 6195 feet to leeward of it. The intermediate inclinations

Table of Inclinations of Waves and Rays.

Coordinates.		Inclination of Wave-front to the Horizontal. θ.		Inclination of Ray to the Vertical. ϕ.		Angle between Ray and Normal to Wave-front. $\phi-\theta$.	
x.	y.						
ft.	ft.	°	′	°	′	°	′
0	0	60		60	34	0	34
1005	500	64	51	66	27	1	36
2383	1000	71	28	73	26	1	58
3359	1250	76	12	77	56	1	44
5059	1500	84	27	85	15	0	48
6195	1547	90		90		0	0

Fig. 3.—Continuous Refraction of Sound by Wind.



of wave-fronts and rays are given in the accompanying table, and graphically exhibited by curve AA of fig. 3, in which the numerals along the axes denote thousands of feet.

(2) Let sound start from the origin, with its wave-front horizontal, then the curve BB (fig. 3) represents the parabolic path described by the ray, the wave-front remaining horizontal throughout. But although the wave-front is never refracted, the ray at a height of 3000 feet has drifted more than 500 feet to leeward. It would, however, never suffer total reflexion, but would asymptote to the horizontal at an infinite height, the ray and the wave-front tending to coincide.

Rays intermediate between AA and BB would suffer total reflexion at greater heights than 1547 feet, and rays below AA at less heights.

University College, Nottingham, Aug. 22, 1900.

XXXIII. *The Anomalous Dispersion of Cyanin.*

By Prof. R. W. Wood *and* Mr. C. E. Magnusson.

[Plates II. & III.]

Attention has been already drawn by one of the present writers*, to the very perfect prisms for the exhibition of anomalous dispersion, that can be prepared by pressing fused cyanin between plates of glass. It was shown to be possible to prepare in this way prisms of any angle desired, with perfect optical surfaces, a thing which it is quite impossible to do by the evaporation method employed by Wernicke and Pflüger. In the same article was given a table of refractive indices for different wave-lengths, and the dispersion-curve in so far as it was studied. At the time of the publication of this paper no satisfactory readings within the absorption-band had been made, owing to the difficulty of pressing prisms of small enough angle to transmit the strongly absorbed rays. Readings within the absorption-band have been made by Pflüger with prisms obtained by the evaporation of an alcoholic solution of cyanin, and the dispersion-curve found to be continuous ; but the surfaces of his prisms were necessarily so imperfect, that it seemed important to repeat the work under better conditions.

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* Wood, Phil. Mag. xlvi. pp. 380-386 (1898).

Since the publication of the paper alluded to above, the work has been continued by the present writers, with still more perfect prisms, very satisfactory readings having been obtained not only in the region of the absorption-band, but also in the ultra-violet.

All previous workers have credited cyanin with but a single absorption-band, the maximum of which is located not far from the sodium lines, but we have found a second band in the ultra-violet beginning at wave-length ·00037.

Two methods have been employed, namely, spectrometer-readings with cyanin prisms, and readings of the displacements of the fringes in a Michelson interferometer produced by thin films of the dye.

A large amount of preliminary work was done on the preparation of prisms. Many dyes were tried, but cyanin seemed to be the only one suitable, consequently the work has been limited thus far to this single substance. The difficulty of squeezing thin enough prisms to transmit yellow light has been already alluded to. Outside of the absorption-band it is possible to work with prisms of angles as large as 15 or 20 minutes. Within the absorption-band a prism of 1 minute angle transmits practically nothing. By using a small screw-press arranged to work within an air-bath kept at the temperature at which cyanin was found to be most fluid, we finally secured some fairly good prisms of the requisite thinness, which was found to be about 30 seconds. It was exceedingly difficult to split off one of the glass plates without shattering the prism, but even this was successfully accomplished, for parts of some of the prisms. The method employed in the determinations of the refractive indices in the visible part of the spectrum was the same as that described in the previous paper, the slit of the instrument being illuminated with monochromatic light obtained from a large direct-vision spectrometer. A portion of this light, made parallel by the collimating lens, passed through the prism, another portion passed through a strip of clear glass immediately adjoining the prism. Two images thus appeared in the telescope—an undeviated, due to the light coming through the clear glass, and a deviated formed by the prism. In this way the effect of any slight prismatic form of the plate-glass was eliminated. The strongly absorbed rays only pass through a very narrow strip bordering the refracting edge of the prism, consequently the image is much broadened by diffraction, and accurate measurements are obtained with great difficulty.

In the following table are given the values of the refractive indices for various wave-lengths obtained with prisms of angles varying from 24 seconds to 17 minutes, something over 80 observations in all. Each one of these observations is the mean calculated from several settings of the spectrometer.

These results are shown graphically in fig. 1 (p. 546), and show conclusively that the dispersion-curve is continuous through the absorption-band.

Measurements in the ultra-violet were made by photography. A Rowland concave grating was used, the slit, grating, and photographic plate being on the circumference of a circle in the customary manner. The slit was illuminated with sunlight in some of the experiments, and by the light of an arc formed between an iron rod and a revolving iron disk in others. A cyanin prism, formed on a quartz plate, with an angle of 2′ 51″·5 was placed between the grating and the plate, at a distance of 177·6 centim. from the latter. This method was employed by Pflüger, and though there are some objections to it, it gave fairly concordant results. A portion of the light from the grating passed through the prism, and a portion through a clear place in the quartz plate. There were thus formed two spectra slightly displaced with reference to one another, and by measuring the distance between corresponding lines, the deviation due to the cyanin prism could be calculated. The lateral displacement was very slight, but by using great care in measuring the shift, fairly accurate values for the refractive indices were obtained. The photographic work was extended into the blue and violet portions of the spectrum, in order that a comparison with the more accurate spectrometer determinations could be

TABLE I.

Prism No. 1, Angle 17′ 3″.

λ.	μ.	λ.	μ.	λ.	μ.	λ.	μ.
7650	1·920	4798	1·387	4610	1·449	4295	1·535
7590	1·970	4792	1·387	4568	1·460	4270	1·533
7350	1·985	4756	1·416	4518	1·479	4191	1·544
7035	2·050	4753	1·401	4442	1·496	4108	1·547
6887	2·131	4727	1·408	4380	1·523	4065	1·557
6856	2·150	4700	1·418	4342	1·524		
4867	1·380	4637	1·434				

Prism No. 2, Angle 4′ 52″.

λ.	μ.
6680	2·232
6581	2·343
5248	1·122
5183	1·154
5142	1·154
5048	1·194
5018	1·266
4958	1·280
4896	1·350

Prism No. 3, Angle 23′ 59″.

λ.	μ.
7320	2·027
6880	2·170

Prism No. 4, Angle 1′ 17″.

λ.	μ.
6636	2·309

Prism No. 5, Angle 24″.

λ.	μ.	λ.	μ.	λ.	μ.	λ.	μ.
6675	2·26	6100	2·14	5890	1·59	5505	1·22
6465	2·35	6070	2·06	5800	1·57	5400	1·12
6335	2·30	6070	1·93	5800	1·59	5182	1·14
6330	2·35	5995	1·86	5680	1·45	5065	1·22
6245	2·33	5970	1·79	5640	1·30		
6100	2·10	5890	1·65				

Prism No. 6, Angle 32″.

λ.	μ.	λ.	μ.
6062	1·88	5610	1·27
5992	1·81	5895	1·58
5180	1·12	5310	1·13
4865	1·33	5183	1·13

Prism No. 7, Angle 51″.

λ.	μ.
6228	2·25
5895	1·67

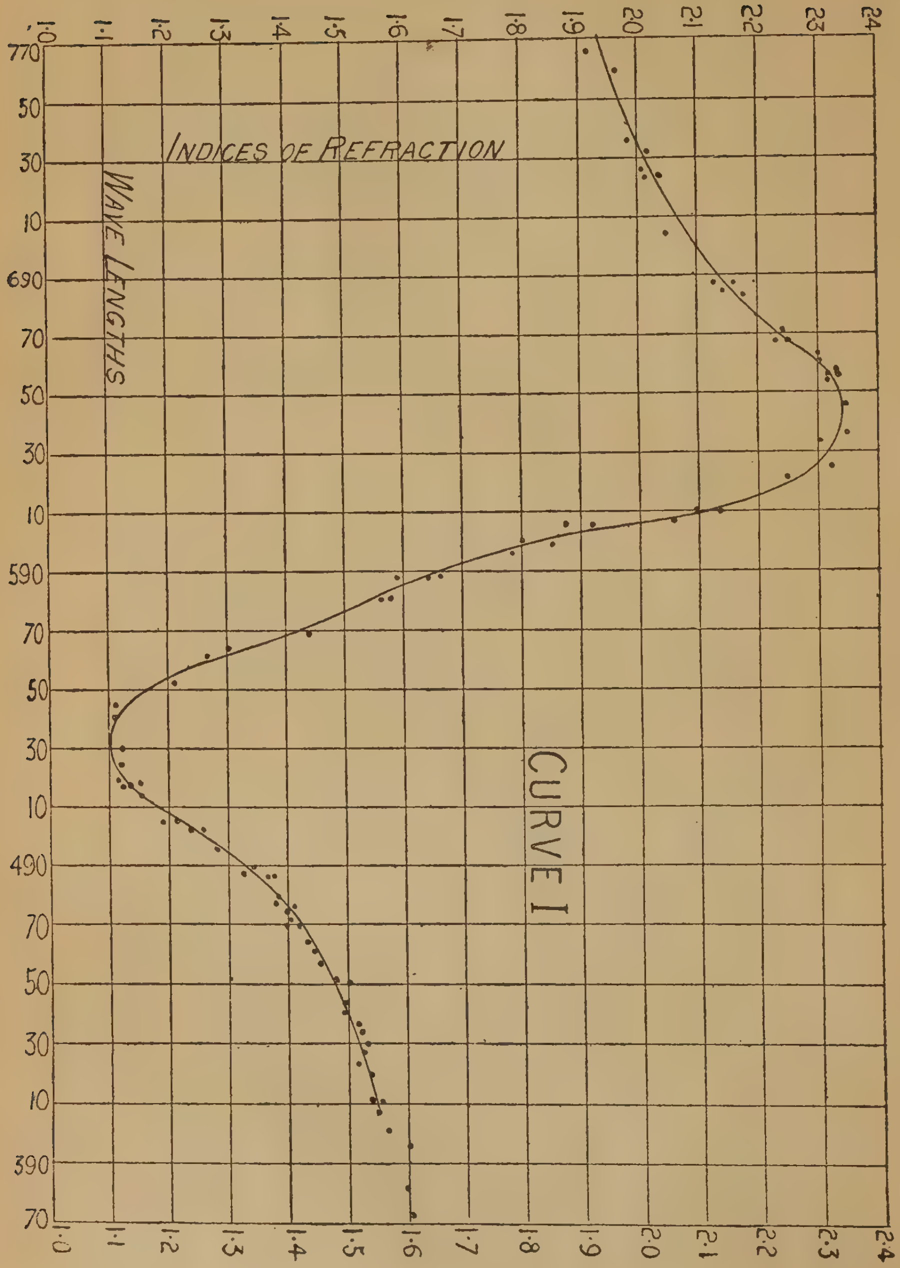
Prism No. 8, Angle 21′ 3″.

λ.	μ.
7236	2·014
7236	2·020
4230	1·507

Prism No. 9, Angle 2′ 10″.

λ.	μ.	λ.	μ.
7230	2·005	5020	1·240
6830	2·190	4865	1·375
6720	2·250	4690	1·40
6570	2·320	4510	1·51
6555	2·320	4410	1·50

Fig. 1.


INDICES OF REFRACTION
WAVE LENGTHS
CURVE I
1·0
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
2·3
2·4
770
50
30
10
690
70
50
30
10
590
70
50
30
10
490
70
50
30
10
390
70

made, and close agreement was found. The results are given in the following table :—

Prism No. 10, Angle 2′ 51″·5.

λ.	μ.
423	1·530
410	1·565
404	1·573
395	1·606
380	1·600
372	1·610

These values, though not shown on the curve, will be found to fit very well.

Beyond wave-length 372 nothing appeared to be transmitted through the cyanin, even with a five-hour exposure, though a strong image of the spectrum transmitted by the uncovered quartz was obtained. Evidently cyanin has a second absorption-band at this point, for the same thing was found in subsequent work with the interferometer, the absorption of glass not beginning until somewhat further along in the spectrum (about ·00033). Whether this absorption extends to the extreme limits of the spectrum has not yet been determined. Pflüger found no traces of this band, and gives values for the refractive index within its limits. It seemed at first that the reason of this might be found in the difference in the optical properties of fused cyanin and that obtained by the evaporation of an alcoholic solution, but we have found that films prepared in the same way as those used by Pflüger show the band also.

By dispersing white light into a horizontal spectrum by means of a glass prism, and then dispersing this spectrum vertically by means of a cyanin prism, the dispersion-curve can be shown objectively. This method of crossed prisms, originally due to Newton, and used by Kundt in his study of anomalous dispersion, is decidedly the best for illustrating the matter to students. Unfortunately it cannot be projected on a large scale, but we have succeeded in photographing it by mounting the prisms in front of a telescope lens of about 2 metres focus. By using the small angle prism the entire spectrum is secured, though the very slight deviation obtained in this case makes the picture unsatisfactory. A number of these curved spectra are shown in Plate II.

The Michelson interferometer furnishes an easy means of determining the retardation of light in thin films of transparent substances, and a somewhat extended study of the dispersion of cyanin has been made with this instrument. It is far easier to obtain thin uniform films of the dye by evaporating the alcoholic solution, than it is to make good prisms in this way: consequently better results were looked for than those obtained by Pflüger with his prisms. The cyanin was deposited from a hot alcoholic solution on selected plate-glass. To secure uniform films in this way, it is necessary to use absolute alcohol and keep the temperature between 35° and 40°, the operation of coating being performed in an air-bath by dipping the plates in the solution and setting them on edge to dry. A uniform film was selected, and one half of the plate was freed from the cyanin, that which remained being bounded by a perfectly straight edge.

The interferometer was adjusted for horizontal fringes, which are most convenient for measuring small displacements, and the plate placed upright before one of the mirrors, with the straight edge bounding the cyanin film perpendicular to the fringes. The central fringe was brought into view by using white light, since it is the only one which can be identified, and furnishes us the only means of telling whether the displacement is half a fringe or a fringe and a half. The interferometer was then illuminated with monochromatic light from the large direct-vision spectroscope, and the double-fringe system photographed for various wave-lengths. "Erythro" plates were used, enabling us to secure records from the extreme red to the ultra-violet, a series of about thirty exposures being made on a single plate. These photographs show the continuity of the dispersion-curve through the absorption-band most beautifully. Beginning in the red we find a large displacement, which increases progressively as we near the region of the absorption-band in the yellow. As soon as we are in this portion of the spectrum, the displacement rapidly grows less, the fringes getting almost into line in the middle of the yellow. Then the displacement begins to increase again as we leave the absorption-band on the blue side, the rate of increase growing less as we near the ultra-violet.

The displacements were measured on the plates by means of a filar micrometer, and were recorded in terms of fringe width. Since the light passes through the film twice, the total displacement is that which corresponds to a retardation of a film of twice the thickness. To calculate the refractive index from the retardation we require the thickness of the film. In order to avoid the many sources of error involved in any attempt to measure the film's thickness directly, we made use of the values already determined for the refractive index for those wave-lengths most freely transmitted by the cyanin. The prism method is the more accurate when reasonably large angles can be used, and the investigations with the interferometer were made with a view of corroborating our results in the absorption-band. Professor Ames has drawn our attention to the fact that in using a prism of a strongly absorbing medium the amplitude of the transmitted wave falls off very rapidly from the refracting edge, and that this might have some effect on the propagation of the wave, for in treating wave propagation we always assume the amplitude to be the same at every point on the wave front. This is a most pertinent suggestion, for if a rapid decrease of amplitude on a wave front changes the position of the effective point to which we can reduce the whole wave (by Huyghens' principle) it should certainly modify to some degree the apparent refractive index as determined by a prism. So far as known no one has ever worked out Huyghens' principle for a wave of variable amplitude. There seems to be no way of making the usual geometrical treatment cover the case, although it seems at first sight as if the method of strip-division might be used.

The interferometer method is not open to this objection however; and the very close agreement between the curves obtained by the two methods, indicates that any possible effect of the variable amplitude is too small to materially influence the results obtained by the prism.

Two of the interferometer series photographs (Plate III.)

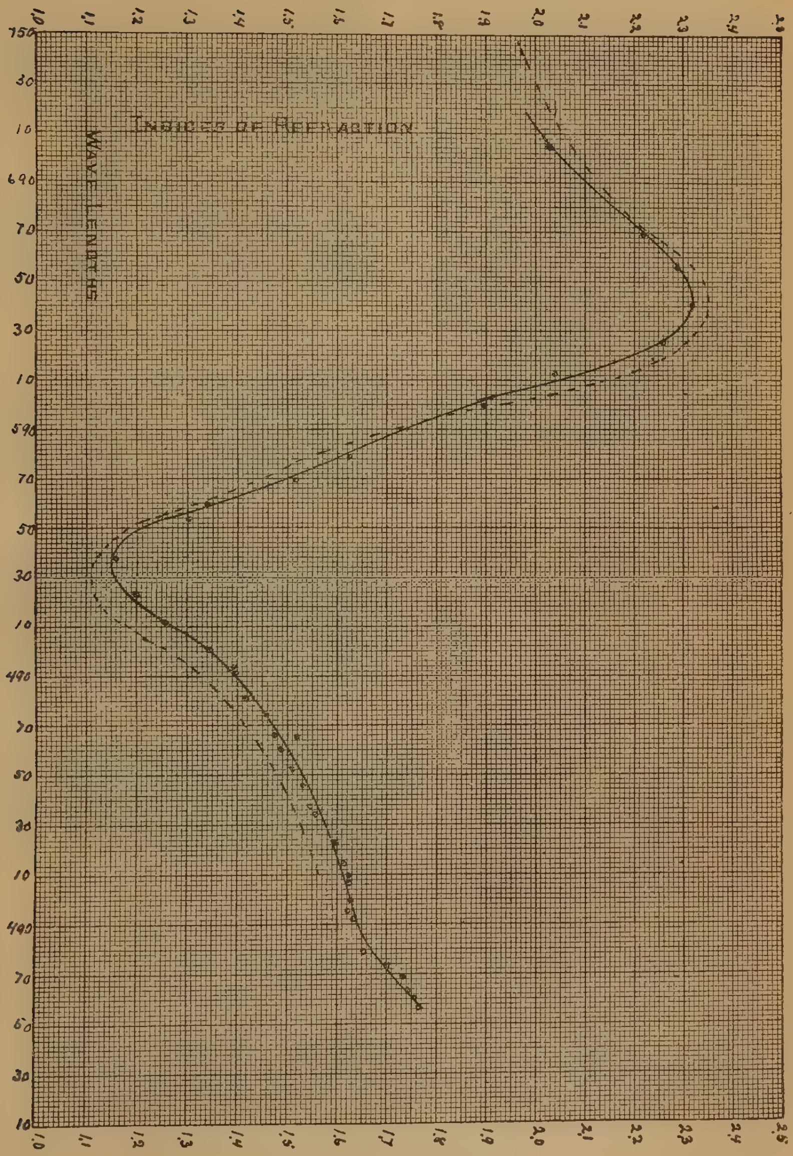
are reproduced, one obtained with a thin film, showing the displacement throughout the region of the absorption-band, and the other made with a thick film, giving much greater displacements, but yielding no fringes in the yellow part of the spectrum. The wave-length of the light used appears below each picture in the series. The two white marks indicate which fringes belong together, and may be taken as giving a rough measure of the displacement. The thickness of the thin film was about 0·00013 millim., that of the thick one 0·00071. One difficulty experienced in measuring the retardation produced by a strongly absorbing film by means of the interferometer is very troublesome, namely, that due to the weakening of one of the interfering beams without a corresponding weakening of the other. This causes a strong and uniformly illuminated field to be superposed on the fringes, and may obliterate all traces of them. It is necessary on this account to use films considerably thinner than would be necessary under other conditions. This difficulty can probably be obviated by a compensation device, and work in this direction is now in progress, with every promise of success. The displacement of the fringes can be doubled by the introduction of a second cyanin film in the other interferometer path, in such a position that the two films are seen side by side in the half-silvered mirror, with their straight edges in contact. This method was not used in the work on cyanin, but has been used successfully by one of the writers in some subsequent work on the retardation caused by thin films of carbon. The introduction of the compensation device will make the method much more accurate, since films several times as thick as those at present used will then be suitable.

The results obtained with the interferometer are shown graphically in fig. 2 (p. 551), forty observations being recorded. The curve obtained with the spectrometer is shown by the dotted line.

In general the two curves agree very well, slight discrepancies being possibly due to a difference in the optical properties of fused cyanin and that obtained by evaporation.

There is decided evidence of a rise towards the ultraviolet absorption band, as there should be theoretically, though we do not regard the values obtained in this part of

Fig. 2.


INDICES OF REFRACTION
WAVE LENGTHS
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1.1
1.2
1.3
1.4
1.5
1.6
1.7
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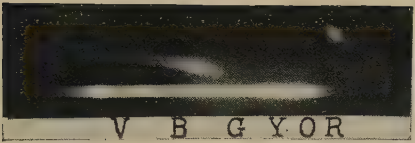
2.0
2.1
2.2
2.3
2.4
2.5
750
30
10
690
70
50
30
10
590
70
50
30
10
490
70
50
30
10
490
70
60
30
10

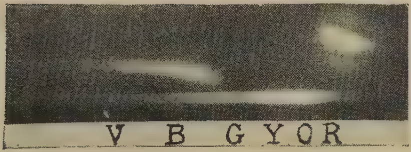
the spectrum as sufficiently accurate to make this point certain. The work in this region will have to be repeated under more favourable conditions.

It was our intention to apply the results of the work to a proof of the Ketteler-Helmholtz dispersion formula, but the discovery of the second absorption-band makes this impossible until the extent of the band has been determined, and the extinction coefficient measured, a matter of considerable difficulty. Some of the discrepancies found by Pflüger between his calculated and observed curves, he thought might be explained by the possible presence of an absorption-band in the remote ultra-violet.

University of Wisconsin,
Madison.



1



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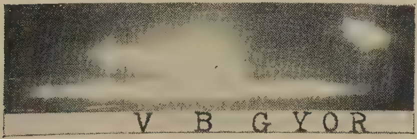

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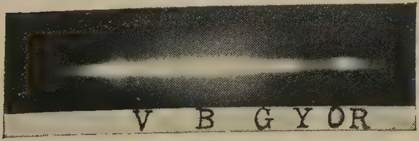

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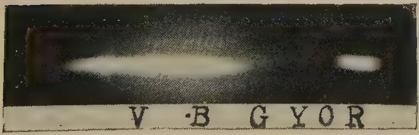

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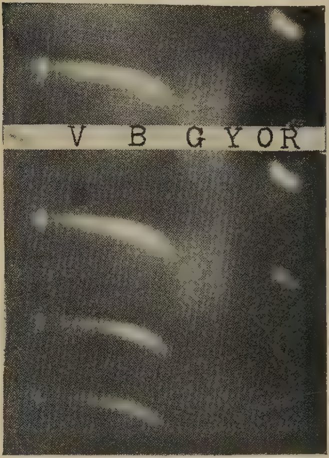


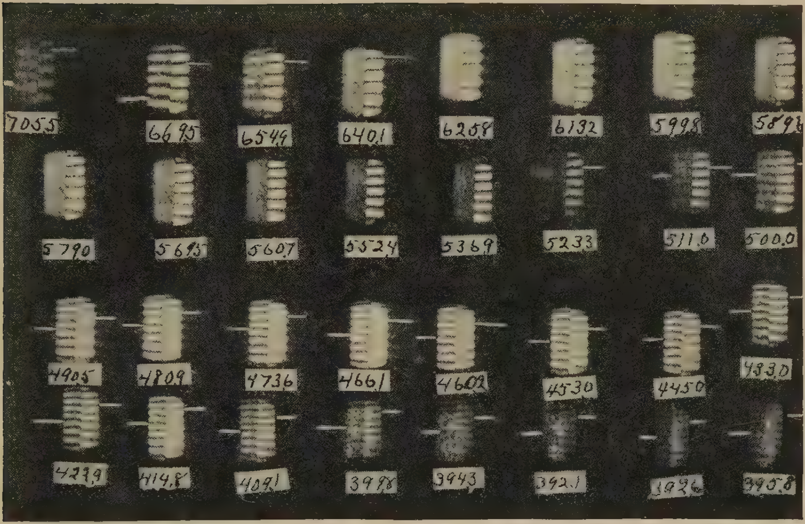
6

No. 1.—Continuous spectrum below. Same deviated by cyanin prism of 17′.

Nos. 2, 3.—Same with prism of 22′. No. 2 taken with Aurantia screen to reduce effect of blue; No. 3 without.

Nos. 4, 5.—Same with prisms of 35″ and 2′ 51″ respectively, showing continuity of curve.

No. 6.—Several exposures with prism of 28′ 30″.


7055
6695
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6401
6258
6132
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589
5790
5693
5607
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511.0
500.0
4905
4809
4736
4661
4602
4530
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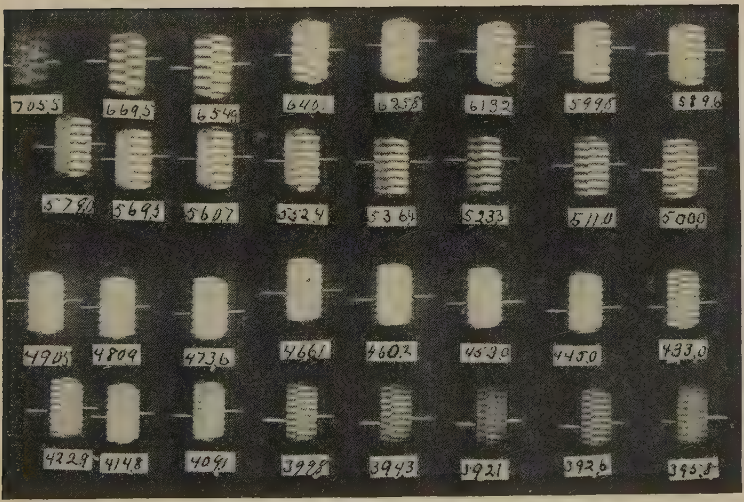
433.0
4229
414.8
409.1
3998
3943
392.1
392.6
395.8

Fig. 1.


7055
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560.7
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5233
511.0
500.0
4905
4809
4736
4661
460.2
453.0
445.0
433.0
4229
414.8
409.1
3998
3943
392.1
392.6
395.8

Fig. 2.

18

XXXIV. *On Astigmatic Lenses.*

By R. J. Sowter, *B.Sc.*, *A.R.C.Sc.*[*]

A lens which so acts on light falling on it as to produce two focal lines in the refracted-ray system is termed an astigmatic lens. Sturm (*Comptes rendus de l'Académie des Sciences de Paris*, t. xx.) investigated the refraction of a circular pencil of light by an asymmetrical surface or lens with circular aperture, and showed that for a convex refracting lens the ray surface was a skew surface (*surface gauche*) bounded by two right lines. Fick (*Mediz. Physik*) has written on the subject; and Knapp (*Archiv f. Ophthalmologie*, Band viii.) has mathematically determined the form of the whole refracted-ray surface. Donders, Reusch, and others have investigated the optical properties of asymmetrical or astigmatic lenses; and more recently Prof. S. P. Thompson has, in his paper on "Obliquely-crossed Cylindrical Lenses,"[†] deduced a very simple geometrical construction for the sphero-cylindrical lens equivalent to two obliquely-crossed cylindrical lenses.

The intent of this paper is to simplify the systematic investigation of the properties of astigmatic lenses, and to show the relation between a general type of astigmatic lens and its equivalents.

The quadric surface is the surface of lowest degree which is capable of representing the general type of thin astigmatic lens. An ellipsoidal lens is here considered as the fundamental form or type. Thin lenses only are treated.

I. *Ellipsoidal Lenses*

A system of parallel and axial rays of light after passing through an ellipsoidal lens becomes a system of rays intersecting in two straight lines. These lines are at right angles, are the focal lines of the lens, and are separated by an interval—the focal interval of Sturm—which depends on the ellipticity of the lens. The focal lines are parallel to the elliptic axes of the lens, and correspond to the lens powers in those directions, *i. e.* to the maximum and minimum powers of the lens. If, in comparing the curvatures of various arcs, a constant or common sagitta is chosen, the curvatures are proportional to the squares of the semi-chords of the arcs; and if the sagitta of an arc is properly chosen, the curvature of that arc is measured by the square of the semi-chord. It follows therefore that the power of a lens or a surface in a given direction can be represented by the inverse square of a length, that length being the semi-chord for the surface in the direction considered. Lens properties may be established by a consideration merely of the arrangement or distribution of refracting material in the lens—by a materialistic method one might say—and this material distribution is determined or indicated by contours of equal thickness. A curve drawn through all points on a lens where the material thickness is equal or constant, may be said to determine a *natural aperture* for the lens. From the natural aperture of a lens the power in any direction of the lens is at once determined, for the power is as the inverse square of the radius vector from the centre of the aperture to the edge in the given direction.

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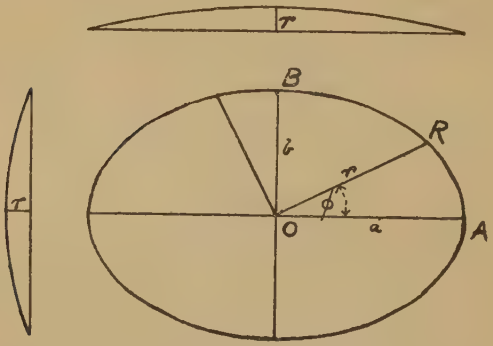
[*] Read November 9, 1900.

[†] Phil. Mag. March 1900; Proc. Phys. Soc. No. 97 (July 1900).

Fig. 1.



An ellipse is the natural aperture for an ellipsoidal lens, and may be taken to represent the ellipsoidal lens.

In the ellipse shown in fig. 1, the semi-axes are a and b, and this ellipse is the natural aperture for an ellipsoidal lens with focal powers, A and B say, where

$$A=\frac{1}{a^2},$$

$$B=\frac{1}{b^2}.$$

The power of the lens in the direction OR (r, ϕ) is

$$R=\frac{1}{r^2}=A\cos^2\phi+B\sin^2\phi,$$

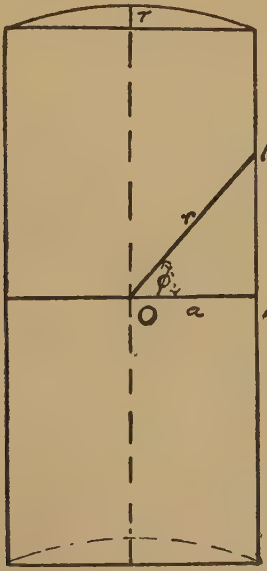
since

$$\frac{1}{r^2}=\frac{\cos^2\phi}{a^2}+\frac{\sin^2\phi}{b^2} \text{ in the ellipse.}$$

It is obvious that the sum of the powers in any two directions at right angles is equal to the sum of the minor and major powers, *i. e.* A + B.

The cornea of an eye affected by corneal astigmatism may be taken as an illustration of an ellipsoidal lens, for the curve of equal thickness or natural aperture for the asymmetrical corneal surface is an ellipse.

Fig. 1 *a*.



For a spherical lens, which is a particular form of ellipsoidal lens, the natural aperture is a circle, the powers are equal in all directions, there is a focus and no focal interval.

A cylindrical lens is a particular form of ellipsoidal lens, it produces only one real focal line and has an infinite focal interval.

For a cylindrical lens the natural aperture is an infinitely long rectangle, fig. 1 *a*, and the lens power in any direction is given by the inverse square of the radius vector.

Thus if A is the equatorial or focal power of the lens and $OA=a$, then $A=\frac{1}{a^2}$.

Also

$$R=\frac{1}{r^2}=\frac{\cos^2\phi}{a^2}=A\cos^2\phi.$$

It is evident then that an ellipsoidal lens may be represented by an ellipse such that the semi-axes are the reciprocals of the square roots of the focal powers, and that a cylindrical lens may be represented by a pair of parallel lines at a distance from an axis equal to the inverse square root of the power of the lens.

II. *Cylindrical Lenses crossed at Right Angles.*

Let two lenses of powers A and B be crossed at right angles, and let the lenses be represented by their natural apertures as in fig. 2.

Then the lens equivalent to the crossed lenses is one in which the distribution of refracting substance is the same as in the combination. This distribution is determined by the natural aperture for the combination.

Now taking the lens axes as axes of coordinates, the equation to the curve of equal thickness, for a thickness equal to the greatest thickness of either lens, is

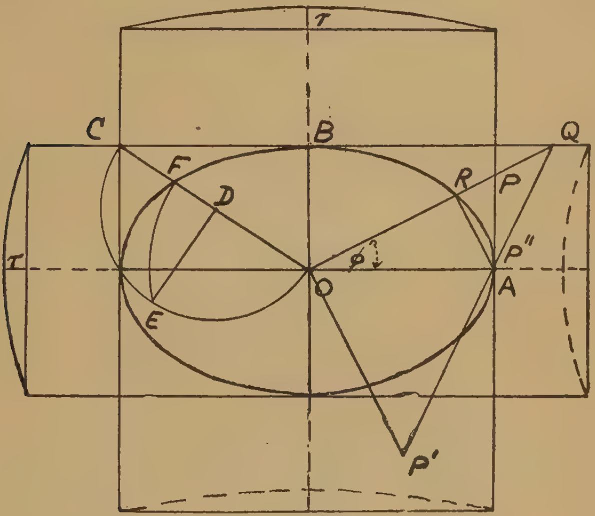
$$Ax^2+By^2=1.$$

The natural aperture is therefore an ellipse, and the combination is equivalent to an ellipsoidal lens with focal powers A and B.

In fig. 2 the lenses represented have powers in the ratio 9 : 4 and are equivalent to the ellipsoidal lens represented by the ellipse inscribed in the rectangle of which the sides are as 3 : 2.

The power of the combination in any direction OQ at an angle ϕ to OA is $\frac{1}{OR^2}$ where OR is the radius vector of the inscribed ellipse, and is also equal to $A \cos^2 \phi + B \sin^2 \phi$.

Fig. 2.



If the lenses are equal, A = B, the ellipse becomes a circle, the power in any direction is A say, and the crossed lenses are equivalent to a spherical lens of power A.

The point R on the ellipse may easily be determined as follows :—

Draw OP′ at right angles to OP and make OP′ = OP. Join Q,P′, and make P′P″ = OP′ = OP, and draw P″R parallel to P′O. Then R is the point on the ellipse, and

$$\frac{1}{OR^2} = \frac{1}{OP^2} + \frac{1}{OQ^2} \text{ for}$$

$$\frac{P'Q}{OQ} = \frac{P'P''}{OR} = \frac{OP}{OR} \therefore \frac{1}{OR} = \frac{\sqrt{OP^2 + OQ^2}}{OP \;\; OQ}.$$

If P and Q coincide as at C, then the point F on the ellipse is found by drawing the semicircle OEC and making OF = OE, where E is the extremity of the radius perpendicular to the diameter OC.

III. *Cylindrical Lenses crossed obliquely.*

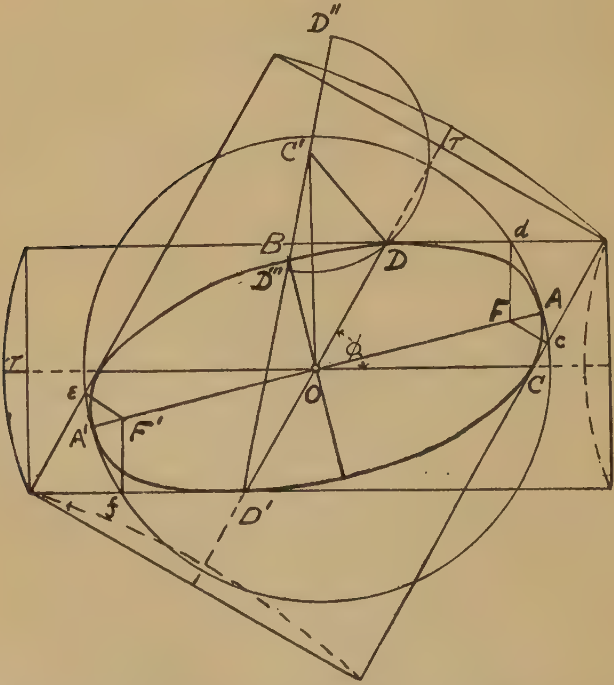
Let the two lenses A and B be crossed obliquely, and let the acute angle between their axes be ϕ.

The curve of equal thickness or natural aperture for the combination is easily determined. The axial thicknesses of both representative lenses are equal, and the equation to the curve for a thickness equal to that axial thickness is

$$A \sin^2 \phi \, x^2 + B \sin^2 \phi \, y^2 = 1,$$

the curve being referred to oblique co-ordinates coinciding with the axes of the lenses.

Fig. 3.



That is, the natural aperture is an ellipse, and the crossed cylindrical lenses are equivalent to an ellipsoidal lens represented by the ellipse inscribed in the parallelogram as shown in fig. 3. The lines OC, OD are semi-conjugate diameters of the ellipse. If the major and minor axes of the inscribed ellipse are $2a$ and $2b$ respectively, then the equivalent ellipsoidal lens is one with focal powers $\frac{1}{a^2}$ and $\frac{1}{b^2}$.

The magnitudes of the axes may be geometrically determined as follows :—

Draw OC′ at right angles to OC, make OC′=OC, join C′D, C′D′, produce D′C′ to D″, making C′D″=C′D, and from C′D′ cut off C′D‴=C′D. Then

$$D'D'' = 2a, \quad \text{and} \quad D'D''' = 2b.$$

To determine the direction of the axes the following procedure may be adopted :—

With O as centre and a length $a=\frac{1}{2}$D′D″ as radius, cut the parallelogram in the points d, c, e, f, and draw dF and cF perpendicular to the sides of the parallelogram to intersect in F. OF is then the direction of the major axis.

To prove the above constructions, let OC$=c$, OD$=d$. Then, since c and d are conjugate,

$$\text{(i.)} \qquad c^2+d^2 = a^2+b^2,$$

$$\text{(ii.)} \qquad cd \sin\phi = ab.$$

Now $\quad DC'^2 = OC'^2+OD^2-2OD\,.\,OC' \cos D\hat{O}C';$

$$\therefore \quad DC'^2 = c^2+d^2-2cd\sin\phi = (a-b)^2$$

by the relations (i.) and (ii.). Therefore

$$DC' = a-b.$$

In a similar manner it may be shown that

$$C'D' = a+b.$$

Hence

$$D'D'' = 2a,$$

$$D'D''' = 2b.$$

Again, the circle $c\,d\,e\,f$ is the locus of the feet of the perpendiculars from the foci on the tangents to the ellipse ; therefore the points FF′ are the foci, and the axes are determined in direction by the line OF.

Analytically a and b are easily determined in terms of

c and d from the equations (i.) and (ii.). Further,

$$\text{(iii.)} \quad \frac{1}{c^2} = \mathrm{A}\sin^2\phi,$$

$$\text{(iv.)} \quad \frac{1}{d^2} = \mathrm{B}\sin^2\phi\,;$$

and from the equations (i.)....(iv.) a and b are readily deduced in terms of A, B, and ϕ.

Thus, since an ellipsoidal lens with powers $\alpha = \frac{1}{a^2}$ and $\beta = \frac{1}{b^2}$ is equivalent to a spherical lens of power α and a cylindrical lens of power $\beta - \alpha$ or $\frac{1}{b^2} - \frac{1}{a^2}$, if C is the cylindricity of the sphero-cylindrical lens, it is easily shown that

$$\mathrm{C} = \frac{1}{b^2} - \frac{1}{a^2} = \frac{\sqrt{(c^2+d^2)^2 - 4c^2d^2\sin^2\phi}}{c^2d^2\sin^2\phi}$$

$$= \mathrm{AB}\sin^2\phi\sqrt{\frac{1}{\mathrm{A}^2\sin^4\phi} + \frac{1}{\mathrm{B}^2\sin^4\phi} + \frac{2}{\mathrm{AB}\sin^2\phi}\left(\frac{1}{\sin^2\phi} - 2\right)}$$

$$= \sqrt{\mathrm{B}^2 + \mathrm{A}^2 + 2\mathrm{AB}(1 - 2\sin^2\phi)}.$$

$$\therefore\ \mathrm{C} = \sqrt{\mathrm{A}^2 + \mathrm{B}^2 + 2\mathrm{AB}\cos 2\phi}\,;$$

and a parallelogram-construction with sides A and B, and angle 2ϕ, as was shown by Prof. S. P. Thompson *, gives the cylindricity in a sphero-cylindrical lens equivalent to two crossed cylindrical lenses, A and B, at an angle ϕ.

The angle of inclination of the cylindrical lens in the sphero-cylindrical combination to the direction OC is the angle between the major axis of the inscribed ellipse and the axis OC.

The equivalence of a sphero-cylindrical combination and an ellipsoidal lens follows at once from the method of contours or apertures. In fact, crossed cylindrical lenses, whether the lenses are at right angles or are inclined obliquely, and also spherical and cylindrical combinations, may be replaced by their equivalent ellipsoidal or quadric lenses, or for an ellipsoidal lens a pair of cylindrical lenses, or a spherical and a cylindrical lens, may be substituted ; for the arrangement

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* Phil. Mag. March 1900; Phys. Soc. Proc. No. 97 (July 1900).

or distribution of refracting substance is similar in such lenses or combinations. And, moreover, the preceding geometrical constructions afford a ready means for effecting the transformation from any assigned type of the combinations named to the type of any other. The method is applicable to astigmatic lenses or combinations in which the curvatures are not all of the same sign.

Discussion.

Prof. S. P. Thompson said he had never seen the treatment of an ellipsoidal lens before. Reusch had deduced the laws of crossed cylindrical lenses from the properties of the paraboloidal lens. The author's method was, so far as he knew, new, and would be very convenient to work with.

XXXV. *The Liquefaction of Hydrogen. By* Morris W. Travers, *D.Sc., Fellow of University College, London**.

22

[Plate IV.]

[*Note by* Prof. Ramsay.—In the course of our researches on the gases of the atmosphere, it became evident that the only means of separating neon in a state of purity from the helium with which it was mixed, was by cooling the mixture of the two gases by aid of liquid hydrogen at its boiling-point under atmospheric pressure. In order to effect this separation, Dr. Travers undertook to design and make an apparatus which would produce liquid hydrogen in quantity; and the following account of the experiments shows that his hopes have been justified.]

The Liquefaction of Hydrogen.

The experiments described in this paper were carried out solely for the purpose indicated in Prof. Ramsay's introductory note. The liquefaction of hydrogen has already been accomplished, and my experiments differ neither in principle nor in conclusions from those of Dewar. Since, however, they show that the production of liquid hydrogen is neither so difficult nor so costly as might have been expected, I have decided to publish an account of them.

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* Read November 23, 1900.

Without touching on controversial matter, the history of the subject may be stated in a few words. In 1884 Wroblewski (*Comptes Rendus*, c. p. 979) showed that when hydrogen, compressed into a capillary glass tube cooled to the temperature of liquid oxygen, was allowed to expand from 100 atmospheres to atmospheric pressure, a sudden appearance of mist or spray in the tube indicated that partial liquefaction of the gas had taken place. In 1895 Olszewski (Phil. Mag. 1895 [5] xl. p. 202) confirmed these experiments by repeating them on a larger scale. Using first a glass tube of 7 mm diameter, and afterwards a steel cylinder lined with glass, from which the gas escaped through a cock, he found that the hydrogen remained in the liquid state for a sufficient time to enable him to determine its temperature by means of a platinum resistance-coil enclosed in the apparatus.

In these experiments the gas which remains in the glass tube or cylinder does work on that part of it which is escaping in overcoming the friction in the cock, the heat generated being carried away by the gas. Were the process truly adiabatic, the fall of temperature inside the apparatus might be calculated approximately from the formula

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}},$$

where p_1 and p_2 are the initial and final pressures, T_1 and T_2 the initial and final temperatures, and k the ratio of the specific heats. The failure to produce any quantity of liquid is chiefly to be attributed to the great difference between the thermal capacities of the gas and of the vessel into which it is compressed.

Lord Rayleigh and Kammerlingh Onnes have suggested independently that it might be possible to liquefy hydrogen by allowing the gas to do work in driving a heat-engine. The cylinder of Onnes's engine is supposed to be constructed of a non-conducting substance of low specific heat and to be enclosed in an insulated space ; a long piston-rod transmits the energy of the system to some mechanism placed outside the apparatus. A mixture of liquid and saturated vapour would escape from the cylinder, and this alone adds to the difficulties to be overcome in constructing the machine.

Lord Rayleigh's suggestion of applying a turbine in a similar manner could be more easily realized.

By either of these processes, if conducted adiabatically, it should be possible to liquefy a *perfect* gas; and we now come to a method which can only be applied to gases which are *imperfect* and show a divergence from the simple gas law.

In the case of a "perfect" gas we may write the equation

$$p_1v_1 = p_2v_2,$$

where pv represents the total energy of the gas. If such a gas were allowed to expand either without doing work or in doing work in such a manner that the whole of the heat generated were absorbed by the gas, no temperature-change would take place in the system. These conditions could be partially realized by allowing the gas to enter a vacuous space through a large orifice, as in Gay-Lussac's experiment, or by forcing it through a porous plug so constructed that the velocity of the escaping gas is reduced to a minimum. The latter method was adopted by Joule and Lord Kelvin, and the results of their experiments show that for all known gases the equation must be written

$$p_1v_1 = p_2v_2 + Q,$$

where Q is the quantity of heat absorbed or generated in performing internal work. In these experiments the gas was compressed by a pump and escaped at constant temperature and pressure through a plug of silk fibre. Work was done on the gas by the pump, and the heat generated $(pv + Q)$ was absorbed by passing it through a coil immersed in water. On its way to the plug the gas flowed in a steady stream, doing no work. In the plug, work was done against friction and the heat generated was absorbed by the gas, so that any temperature-change which occurred could be considered as consequent on the performance of internal work only. If the gas were allowed to escape at a jet, instead of passing through a plug, it is possible that, even in the case of a perfect gas, a fall of temperature would occur close to the jet owing to the conversion of molecular energy into kinetic energy: the effect would, however, be entirely local, and would disappear as the velocity of the stream was reduced in the formation of eddies. The results of Joule and Lord Kelvin, and of others of a more recent date, show that in the case of the commoner gases a fall of temperature takes place on free expansion. With hydrogen, however, and probably with helium also, the temperature rises; these gases being, to use Regnault's expression, "plus que parfait."

It was first suggested by Hampson in England and Linde in Germany, that the principle of free expansion might be applied to the liquefaction of air. In the Hampson-Linde process the compressed air *flows* through a coiled copper tube, and expanding at a jet becomes cooled. The expanded gas passes back over the outside of the coil, losing any velocity it may have attained in forming eddies, so that any external work done results in the formation of heat which is absorbed directly by the gas. The effective cooling is the result of the work done against internal stresses only; and since the temperature of the expanded gas is lower than that of the coil, the latter together with the compressed gas it contains becomes cooled.

Within the last two years Dewar has shown that at a temperature close to −200° C. hydrogen also behaves as an *imperfect gas* and becomes cooled when suffered to expand freely. His experiments, which are described in the 'Chemical News' for March 1900, led him to apply this discovery to the liquefaction of hydrogen in quantity, and this he has successfully accomplished. The details of the method employed have not however been published.

Since there has been some confusion in dealing with the subject, it may be well to point out once more here that there is an essential difference between the processes employed by Olszewski and Dewar. There is no cooling of the gas *in the coil* of the Dewar apparatus owing to the performance of work; this is done entirely by the pump, and the gas merely flows along the tube in a steady stream and transmits the pressure to the jet. The cooling must be attributed entirely to the performance of internal work consequent on change of volume only. In Olszewski's experiments the pressure in the cylinder is not maintained, and work is done by the gas which it contains.

The temperature at which the Joule-Thomson effect for hydrogen changes sign has yet to be determined; it probably lies very low.

I shall now proceed to describe my own experiments. In a preliminary experiment the gas, under a pressure of two hundred atmospheres, was cooled to −80° C. by passing through a coil immersed in a mixture of carbonic acid and alcohol, and was then allowed to expand at the jet of a Hampson air-liquefier, the coil of which had previously been cooled to the temperature of liquid air. Under these conditions it appeared that progressive cooling did not take place, and it may be concluded that at −80° C. hydrogen is still a *perfect gas*.

Four attempts were made to liquefy hydrogen before an apparatus was constructed which gave satisfactory results. These experiments, which occupied about three months, I shall not describe; it suffices to state that they served to show that hydrogen remains a *perfect gas* down to very low temperatures.

The details of the structure of the apparatus finally employed in liquefying hydrogen are shown in Plate IV.; text-fig. 1 indicates the general arrangement of compressor, &c.

The hydrogen from the compressor under a pressure of 200 atmospheres enters the liquefier through the tube, and passes through a coil A, which is cooled to −80° C. in a mixture of solid carbonic acid and alcohol. It then enters the coil contained in the chamber B, which is continually replenished with liquid air during an experiment. The lower portion of this coil passes into the chamber C, which is closed and communicates through the pipe *ff* with an exhaust-pump; liquid air flows continuously from B into C through a pin-valve, controlled by a lever *b*, and boiling under a pressure of 100 mm. of mercury lowers the temperature to −200° C. The gas now passes into the regenerator-coil D which is enclosed in the vacuum-vessel H, and, expanding at the valve E, passes upwards through the interstices of the coil and the annular space F, surrounding B and C, to the outlet G, whence it can return through w and R and the cock i to the main supply-pipe N. The liquid which separates from the gas is ultimately collected in the vacuum-vessel K, which can easily be removed.

In constructing the apparatus the coil D was wound on the thin steel tube c which contains the valve-rod. The latter is screwed at its lower end into a perforated brass cylinder, soldered to the end of c, enclosing the expansion-jet. By turning the milled head a, the width of the annular space between the jet and the end of the valve-rod can be accurately adjusted and the flow of gas controlled. This valve was made for me by Brin's Oxygen Company after the pattern of Dr. Hampson, who first applied it in his apparatus for liquefying air. To the use of this form of valve I must attribute the success of the work, for, unlike the pinhole-valve, it does not become blocked with the impurities which separate from hydrogen obtained by treating commercial zinc with sulphuric acid. The coil itself consists of 80 feet of solid drawn copper tube of $\frac{5}{64}$ inch internal and $\frac{9}{64}$ in. external diameter; in winding it the spirals ran alternately away from and towards the central tube, and great care was taken to preserve a uniform external diameter of $2\frac{3}{4}$ inches. The coils were carefully spaced and fixed in position with solder as each layer was wound.

The length of the regenerator-coil D was 7 inches; and it must be pointed out here that in absence of all quantitative knowledge as to the behaviour of hydrogen at low temperatures, the choice of this dimension was a matter of guesswork; it was found, however, to be sufficient.

The next step in the construction of the apparatus was to fix the flanged plates d and e, which form the top and bottom of the chamber B, onto the tube c. The coil passes through both these plates, and e is also pierced for the passage of the exhaust-pipe f and for the liquid-air valve which is controlled by the rod b; the latter is screwed through a block fixed to the upper surface of e, so that by turning c the conical point closes to a greater or less extent the hole in the plate. All these junctions were made with hard solder; the tube g, which fits exactly over d and e, was then fixed in position with soft solder.

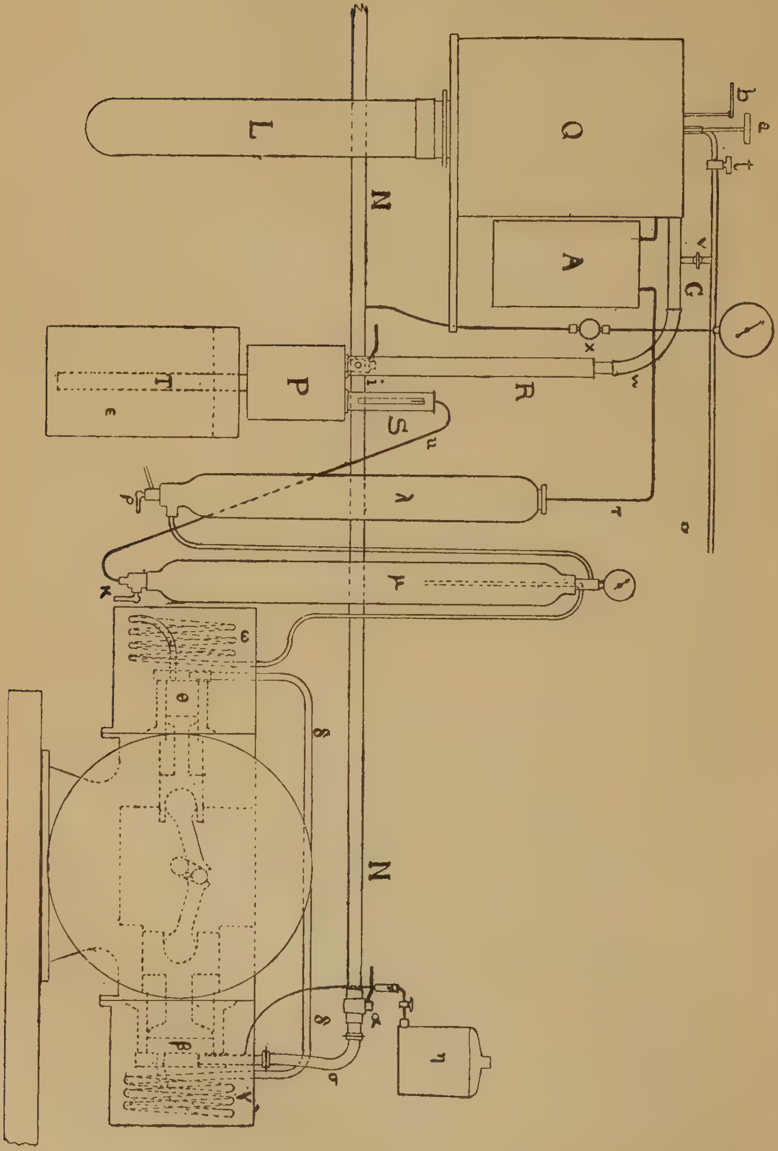
To allow of the escape of the hydrogen gas after its passage through the coils, a brass tube *k* of the same external diameter as the coil was fitted at the top to *g* by means of a collar soldered to both tubes, and supported by distance-pieces at the bottom. The annular space F so formed communicates with the escape-pipe G, as shown in the figure and section; the cold gas passing through F forms an excellent insulator for the liquid-air chambers B and C.

To support the whole apparatus, and to afford a means of securing the vacuum-vessel H, a collar *l* is soldered to the tube *k* and to a tube *m* 4 inches in diameter, which rests on a flange *n* in a hole in a shelf attached to the wall of the compressor room. The space between *m* and *k* is packed with animal wool, as is also the space within the containing-cylinder Q.

The vacuum-vessel H is of such a diameter that when the coil B and the tube *k* are covered with a single layer of flannel it exactly fits over them. To make a gas-tight junction a rubber ring, which fills the space between the vacuum-vessel and the inner wall of *m*, is pressed between a brass ring *o* and a gland *p*. The ring *o* rests on three short studs on the inside of *m*, and the gland is forced home by three nuts and screws *q q* which are fixed at their upper ends into the flange *n*.

When the gland is in position the only means by which gas or liquid can escape from the apparatus is by the tube G, or through the opening at the bottom of the vacuum-vessel H. It is, of course, intended to draw off the liquid at the latter opening, and as it is quite impossible to employ a stopcock for the purpose, the following arrangement has been adopted. The vacuum-vessels H and K are both enclosed in a glass tube LL, which is closed at the bottom and is connected at the top by a rubber sleeve *s* to a brass tube *h* which forms part of the gland *p*; a short copper tube is soldered into *s* and terminates in a stopcock *r*. When *r* is closed any liquid formed at the valve E is retained in H; but when *r* is opened the liquid can flow into K, as the gas produced by its evaporation can then escape. The lower part of the tube L is enclosed in a large vacuum-vessel M, which contains a small quantity of liquid air during the experiment; it serves rather to

Fig. 1.



prevent the frosting of the outside of L than to exclude heat.

The hydrogen escaping from G passes through the rubber tube *w* into the tube R, which communicates directly with the cylinder P (text-fig.) and through the stopcock *i* with the main supply-pipe N connecting the gasometer and the compressor. The cylinder P is of sheet zinc, and is soldered to the three brass tubes R, S, and T. The tube S, which is lined with glass and has a window in front and behind, contains the nozzle of the tube leading from the cylinder μ in which the water used to lubricate the cylinder of the compressor is separated; this arrangement prevents the loss of the gas which escapes each time the water is discharged. The tube T reaches to the bottom of a deep vessel (fig. 1, ϵ) filled with water; it serves also as an escape for the gas issuing from G before the cock *i* is opened.

The tube *f* communicates with an exhaust-pump which is not shown in either figure. It is a simple double-action pump with a single cylinder of 3-inch bore and 6-inch stroke, and, driven by a half-horse-power gas-engine, maintains a vacuum of 100 mm. of mercury in the chamber C. The barrel and plug of the stopcock *t* are bored so that C can be cut off from the pump and opened to the air; through the stopcock *v* the pipe G can be placed in communication with the pump.

It is now convenient to call attention to the general system of heat-insulation in the apparatus. The coil A is surrounded with solid carbonic acid and alcohol, contained in an earthenware battery-jar which is unprotected; the tube between A and B is surrounded with a wrapping of animal wool and covered with baize. B and C are protected by the cold gas returning through the annular space F after passing through the regenerator-coil D; additional protection is afforded by the layer of animal wool inside the cylinder Q. The increasing steepness of the temperature-gradient at C is compensated for by the protecting influence of the upper part of the vacuum-vessel H; the vacuum-vessel M, which contains liquid air, serves as a protection to K and the lower part of the regenerator-coil D; it also prevents deposition of moisture on the tube L. The method of supporting the apparatus by the tube m answers admirably, for as the space between m and κ is packed with wool, the gland p only becomes frosted over when the experiment is at an end, showing that the influx of heat in this direction is inconsiderable.

The hydrogen gas was obtained by the action of dilute sulphuric acid on commercial granulated zinc, and was stored in a gasometer over water. The gasometer consists of a cylinder of sheet iron (No. 16 gauge), 6 feet in height and 5 feet 6 inches in diameter, inverted in a cylindrical tank which was filled with water. The gas enters and escapes through a 2-inch iron pipe, passing through the bottom of the tank and terminating inside a small dome 6 inches in diameter on top of the inner cylinder. This arrangement makes it possible to expel the whole of the gas from the gasometer without danger of introducing water into the supply-pipe. Before filling the gasometer the water in the tank is saturated with hydrogen by passing a stream of the gas through a tube reaching to the bottom. This operation occupies about five days.

The main bulk of the hydrogen is generated in the following manner. About 40 lb. of zinc are placed in a beer-cask fitted with a tap-funnel, a delivery-tube, and an escape-pipe, which passes into a vessel filled with water and so acts as a safety-valve; there is also a stoneware cock at the bottom for drawing off spent acid. When all the air has been expelled from the cask the gas, after passing through a wash-bottle filled with a solution of potassium permanganate, is allowed to enter the gasometer. The latter is thoroughly *washed out* with hydrogen before the main quantity is collected. The preparation of the hydrogen occupies five hours.

The general arrangement of the plant for the compression of the hydrogen, which is carried through the pipe NN to the cock and temporary communication made by means of a lead pipe σ with two screw-unions, is shown in text-fig. 1. The hydrogen, or air when the latter is to be liquefied, is first of all taken into the low-pressure cylinder β of the compressor, which is driven by a 5-horse-power motor, and passes thence through the coil, kept cool by a current of water which circulates through the tanks surrounding the cylinders and coils, and enters the high-pressure cylinder through the tube δ under a pressure of about 16 atmospheres. A small quantity of a mixture of glycerol and water containing 5 per cent. of caustic soda is taken into the low-pressure cylinder together with the gas. The mixture is contained in the vessel η, and the flow is controlled by the glass stopcock and arrangement shown in the figure. In the second cylinder θ the pressure is raised to about 200 atmospheres, and the gas, after passing through the coil ω, enters the cylinder μ, in which the water used in lubricating the cylinders is separated and expelled through the cock κ. This water, together with a little gas, passes along the tube u and enters the cylinder P: the water flows into the tank ϵ, and the gas, during the compression of the hydrogen, is allowed to return to the gasometer through the cock i. The details of this apparatus have already been given.

The gas from μ passes into the cylinder λ, which contains lumps of solid caustic potash to remove traces of moisture or of other impurities. This cylinder is employed in compressing both air and hydrogen, and can be connected by the tube τ either with a Hampson air-liquefier or, as in the figure, with the coil A of the liquid-hydrogen apparatus. The tube τ also communicates with a gauge and with a cock, through which, if the pressure becomes too high, the excess of gas may be allowed to escape into the pipe NN connecting the gasometer and the compressor. The liquefier, of which the detail has already been given, does not require further description. It is sufficient to state that the gas, after passing through the coils enclosed in Q and L, expands at a valve within L controlled by the milled nut a, and finally returns by the tubes G, w, and R and the stopcock i to the tube N.

The loss of gas during each experiment amounts to about 10 per cent. of the whole; and since air and other gases of higher boiling-point separate as solids in the vacuum-vessel H, the gas becomes purer each time it is used.

During the two or three days immediately preceding an experiment, the compressor is employed in producing liquid air. For this purpose we use a Hampson liquefier, which is capable of yielding about 1·25 litres of the liquid per hour The liquid air is stored in vacuum-vessels capable of holding altogether about 8 litres; comparatively little loss occurs through evaporation, and the vessels are usually filled up on the last morning. After preparing the liquid air it is advisable to take the compressor to pieces and carefully inspect the valves, springs, and fibre packings. In the meantime the Hampson machine is removed, the connexions are made between the potash cylinder and the hydrogen liquefier, and the lead pipe connecting the supply-pipe NN with the intake of the compressor is placed in position.

The actual experiment requires four persons. One controls the valves *a* and *b*; the second attends to the compressor, regulates the escape of the water from the cylinder μ, and opens or closes the cock *x* as the pressure rises or falls; the third sees that the vessel in which the coil A is immersed contains sufficient solid carbon dioxide; the fourth hands the vacuum-vessels of liquid air as they are required.

The first step in the operation is to cool the liquefier to the temperature of liquid air. Liquid air is first poured into the chamber B, and thence flows into C by connecting it with the exhaust-pump through the cock *t* and turning the valve *b*; when C is partially filled and the vacuum-gauge indicates that the liquid air is not evaporating at a great rate, the valve *b* is closed and the cock *t* is turned so as to cut off the exhaust and leave the chamber open to the atmosphere (p. 565).

The vacuum-vessel M and the tube L with the vacuum-vessel it contains are removed by rolling up the rubber sleeve *s* on to the tube *h* and lowering the cradle in which M is suspended. The rubber cap carrying the tap *v* is then fitted to the nozzle of H and connected with a rubber tube dipping into a vacuum-vessel filled with liquid air.

The escape-pipe G, from which the rubber tube has already been removed and replaced by a rubber cork, is now connected with the exhaust-pump through the cock *v*. Liquid air is drawn into the vacuum-vessel H, and on closing the stopcock V boils under reduced pressure, cooling the regenerator-coil to below −200° C. By closing the cock *v*, removing the rubber cork, and opening the stopcock V, the liquid air flows out of H. The rubber cap securing V is now removed, the tube L and the vacuum-vessels M and K are replaced in position, and the rubber sleeve *s* is secured to L with a single turn of copper wire.

Meanwhile the assistant in charge of the compressor has removed all air from the compression-apparatus by opening the cock α (text-fig. 1), allowing the compressor to make a few revolutions and then stopping it and opening the cock ρ. This operation is repeated three or four times; the pressure is then allowed to rise, the valve a being closed, and the gas is allowed to escape, if necessary, through the cock x into the pipe N. The arrangements are made so that the pressure is raised to 200 atmospheres by the time the liquefier has been cooled and the vacuum-vessels K, &c., replaced.

The remaining operations may be shortly described:—

Communication is once more established between the chamber C and the exhaust-pump, and the valve b is carefully regulated so that the liquid air does not enter too fast; a too rapid flow is at once indicated by a fall of the mercury in the vacuum-gauge. The expansion-valve is then opened by turning the milled nut d, and the gas, passing upwards through the coils, through the annular space F, through the tubes G, w, and R, finds its way into P, and is allowed for a few moments, in order to remove air from the apparatus, to escape through the water in the tank ϵ. The cock i is then opened, and the gas is allowed to circulate through the system. The chamber B and the vessel containing the coil A are continually replenished with liquid air and solid carbonic acid respectively.

The whole difficulty in this part of the experiment lies in properly regulating the escape of the hydrogen. The rate of flow of the gas is roughly indicated by the height of the glycerol in the gauge z, which shows the pressure in the interior of the apparatus caused by the friction of the gas in the tubes G, w, and R. It is intended in future experiments to introduce in place of w a coil of lead pipe, and to connect the top of the glycerol gauge with a tube leading into the cylinder P, as it will then give an absolute reading of the rate of flow of the gas.

The reasons for which it is necessary to carefully regulate the valve are twofold. Firstly, the hydrogen must not pass too quickly through the refrigerating-coils else the gas is insufficiently cooled; secondly, since liquid hydrogen has a very low specific gravity, the gas and liquid do not separate readily at the jet, and much of the latter is lost. Further, since the efficiency of the regenerator-coil is dependent on the rate of transmission of heat through its walls—and this is proportional to their superficial area—the maximum effect is attained with a limited quantity of gas.

To guard against blocking of the valve by the deposition of solid impurities, the milled nut *a* is turned slowly backwards and forwards during the whole experiment. In the valve E the screw fits so tightly into the brass cylinder containing the jet that no gas can escape from the liquefier through the steel tube *c*, and it is necessary at times to apply some force to *a*. In constructing another machine I should either place the screw on the valve-rod in the tube *c* about two inches above the valve, or I should ease the screw in its socket and place a gland round the valve-rod at the top of the steel tube *c*.

There appears to be no danger of the coil becoming blocked through the deposition of solid matter inside it, even though the hydrogen contains two or three *per cent.* of air and perhaps traces of arseniuretted hydrogen, hydrocarbons, &c. It must be remembered that within the regenerator-coil, even very close to the jet, the temperature of the gas does not fall below its critical point or the coil would become filled with liquid, and it appears that this is not the case. Under these conditions a gas is capable of holding a considerable quantity of solids *in solution*, a phenomenon which has not been fully explained; this may account for the fact mentioned above. Solid impurities do, however, separate from the liquid in the vacuum-vessel H, but as the liquid on its way to the vessel K is obliged to pass through a piece of baize pressed down into the bottom of H by a spring, it can be collected perfectly clear.

Almost immediately the valve E is opened the inside of the vacuum-vessel H becomes coated with a layer of white matter, which is probably solid air; and shortly after, placing a light behind the lower part of the apparatus and opening the cock *r*, liquid is seen running in a fairly rapid stream from the nozzle of H and collecting in K. The flow of the gas from the jet E can then be checked, the tubes M and L lowered, and the vacuum-vessel K, which is attached to a wire, withdrawn and placed in another vessel containing a little liquid air. It would then be possible to place another vacuum-vessel in L, to restore L and M to their original positions, and to prepare a further quantity of liquid hydrogen ; this has not, however, been attempted.

The apparatus which I have described, with the exception of the compressor, motor, and Hampson air-liquefier, which together cost about £200, is comparatively inexpensive. The gasometer cost £15, the material used in making the liquefier amounted to about £5, and possibly £30 was spent in the experiments in addition to the sum named. Each time liquid hydrogen is made 5 kilos of solid carbonic acid and 8 litres of liquid air are used ; this involves a further cost of about £1. These figures indicate that the cost of liquid hydrogen is not excessive.

I am much indebted to Mr. Holding, lecture-assistant in the department, for assistance in constructing the liquefier and in carrying out the experiments. I also wish to express my most cordial thanks to Dr. W. Hampson for his valuable advice and for the assistance which he has so willingly rendered.

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Discussion.

Dr. Hampson said he would like to offer a correction. Dr. Travers had said that he (Dr. Hampson) was the first to liquefy air by the application of the counter current process to the Joule-Thomson effect. Although he was the first to make the proposal, he was not the first to apply it. Dr. Travers had referred at length to a valve which he (Dr. Hampson) had devised, but as it was straightforward common sense he did not wish to accept any credit for the use it had been to the author in his experiments. He would like to call attention to the remarkable features of the work in two respects :—The economy of means and the magnitude of results. By means of liquid hydrogen Prof. Ramsay and Dr. Travers had succeeded in obtaining the physical and other properties of some of the rarer gases.

Prof. S. P. Thompson said the author had asserted that the Joule-Thomson effect for hydrogen changes in sign at some temperatures, and expressed his interest in the fact that it was possible to get a cooling effect by allowing hydrogen to expand.

Mr. Boys asked if it was necessary or desirable to allow the hydrogen to expand to atmospheric pressure.

Dr. Travers said the mechanical advantages of this were great.

Dr. Lehfeldt asked if there had been any attempt to determine the temperature of the liquid, and, secondly, if the apparatus could be employed to determine the magnitude of the Joule-Thomson effect.

Dr. Harker asked if the temperature at which the Joule-Thomson effect changes sign was known.

Dr. Donnan said that the effect changed sign at the temperature at which "*pv*" was a minimum.

Dr. Travers, in reply to Dr. Lehfeldt, said he had not determined the temperature of the liquid, and the apparatus was not suitable for measuring the Joule-Thomson effect. He should say that the change of sign occurred about −150° C. It was Daniel Berthelot who first pointed out that the change of sign corresponded with the minimum value of "*pv*." In the experiments of Amagat the gas was obtained by heating potassium formate and probably contained as much as 30 per cent. of carbon monoxide; the results were not sufficiently accurate to give the temperature.

XXXVI. *Electromotive Force and Osmotic Pressure.*

By R. A. LEHFELDT *.

IN a communication read before the British Association at Dover † I drew attention to a difficulty in the interpretation of the ordinary (logarithmic) expression for the electromotive force between a metal and solution. The following ‡ is an attempt to supply some explanation of the difficulty there raised.

(i.) *Electromotive Force of a Concentration-cell calculated Thermodynamically.*

The simple case of a cell made up of metal : dilute electrolyte : concentrated electrolyte : metal, in which the electrolyte is regarded as completely dissociated, has frequently been treated by the thermodynamic method of the cyclic process, and yields, as is well known, the result

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* Read November 9, 1900.

† Sept. 1899. Printed in the Phil. Mag. (5) vol. xlviii. pp. 430–433 (1899), and *Zeits. f. phys. Chem.* vol. xxxii. p. 360 (1900).

‡ *Note.*—After reading the above-mentioned short paper at the British Association, it occurred to me that the answer to the question there raised probably lay in the inapplicability of Boyle's law to strong solutions of electrolytes. I then worked out the piece of thermodynamical theory given in the present article, but held it over till the completion of the experiments undertaken. Since then Dr. S. R. Milner has published an interesting communication (Phil. Mag. May 1900) written from the same point of view, and partly anticipating the theory given below. I have nevertheless thought it worth while to publish this paper in its original form, as the deduction differs in certain respects from Milner's. In thermodynamic arguments about osmotic pressure, it is apparently indispensable to make use of the conception of a semi-permeable partition; but I think it is highly important to make the assumption of such a partition harmonize as closely as possible with experimentally practicable processes. Milner assumes a membrane permeable to anion (NO_3), but not to cation (Ag), and then by a reversible cycle deduces an equation similar to (3) below.

Such a partition would of course set up an electromotive force between two solutions of different concentrations; but the E.M.F. so obtained is not identical with that of the actual fluid-contact in a concentration-cell, as reckoned by Nernst and Planck. No such partition has yet been discovered, and it is doubtful whether it could exist; and therefore I think doubts may well be cast on processes of reasoning based on its assumption. In my own deduction I have followed out a cycle which appears to me of a more natural kind, and assumed only a partition possessing properties similar to those observed in the case of copper ferrocyanide.

$$E = RT\,\frac{(1-x)n}{r\epsilon}\log\frac{C_2}{C_1}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E = electromotive force,
R = gas constant,
T = absolute temperature,
x = transference ratio for the cation,
n = number of ions formed from molecule of electrolyte,
r = least common multiple of the valency of the ions,
ϵ = quantity of electricity associated with 1 gram-equivalent of an ion,
C_1 C_2 = concentration of the weaker and stronger solutions respectively,

the electrode in the weaker solution being the anode.

Now let us take a step nearer to the actual circumstances, and consider the same cell with the electrolyte dissociated incompletely, viz. to an extent γ_1 in the anode vessel, γ_2 in the cathode vessel.

We may carry out a cyclic process at constant temperature as follows :—

(1) Let a quantity δH of electricity flow through the cell from anode to cathode. Then $\frac{\delta H}{\epsilon}$ equivalents of metal dissolve at the anode, the same mass is deposited on the cathode, and at the boundary between the two solutions $x\frac{\delta H}{\epsilon}$ equivalents of metal are transferred with the current $\frac{(1-x)\delta H}{\epsilon}$ of acid radical in the opposite direction.

The anode vessel therefore gains $\frac{(1-x)\delta H}{\epsilon}$ equivalents of each ion or $\frac{(1-x)\delta H}{r\epsilon}$ mols. Now it will somewhat simplify the explanation without any loss of generality, if we assume that the anode and cathode vessels each contain unit volume (1 c.c.) of solution. Then the anode vessel contains C_1 mols.

of salt, and the change in that quantity is

$$\delta C_1 = \frac{(1-x)}{r\epsilon}\,\delta H.$$

Similarly,

$$\delta C_2 = -\frac{(1-x)}{r\epsilon}\,\delta H.$$

The work done by the cell in this process is

$$E\,\delta H = \frac{Er\epsilon}{1-x}\,\delta C_1.$$

(2) Place the anode solution in a cylinder closed by a piston permeable to water but not to salt (whether dissociated or not), and allow the solution to fall in concentration to the original value C_1. The work done by the solution is $P_1 \delta V_1$. To evaluate δV_1 the change in volume, we have

$$\frac{\delta V_1}{V_1} = \frac{\delta C_1}{C_1};$$

but since $V_1 = 1$,

$$\delta V_1 = \delta C_1 / C_1.$$

To evaluate P_1 we will *assume that the gaseous laws hold* for the solution: then

$$P_1 = RTC_1\{1 + (n-1)\gamma_1\}.$$

Hence the work done is

$$RT\{1 + (n-1)\gamma_1\}\delta C_1.$$

(3) In a similar manner, concentrate the cathode solution reversibly till it recovers its original strength: the work done by the cell is

$$RT\{1 + (n-1)\gamma_2\}\delta C_2 = -RT\{1 + (n-1)\gamma_2\}\delta C_1.$$

We have now, however, more anode solution than was originally present; therefore we must—

(4) Separate $\frac{\delta C_1}{C_1}$ cubic centimetres of the anode solution, concentrate them reversibly till they attain the strength of the cathode solution, and add them to the cathode solution. The work done by the solution in this process (negative) is

$$\int P dV,$$

where

$$dV = -V\frac{dC}{C} = -\frac{\delta C_1}{C_1}\cdot\frac{dC}{C},$$

and

$$P = RTC\{1+(n-1)\gamma\};$$

therefore the work

$$= -\delta C_1\int_{C_1}^{C_2}\frac{RT}{C}\{1+(n-1)\gamma\}dC.$$

Since the total work in the cycle must be zero, we find :—

$$\frac{Er\epsilon}{1-x}\delta C_1 + RT\{1+(n-1)\gamma_1\}\delta C_1 - RT\{1+(n-1)\gamma_2\}\delta C_1$$
$$-\delta C_1\int_{C_1}^{C_2}\frac{RT}{C}\{1+(n-1)\gamma\}dC = 0,$$

or

$$E = \frac{RT(1-x)}{r\epsilon}\left[(n-1)(\gamma_2-\gamma_1) + \int_{C_1}^{C_2}\{1+(n-1)\gamma\}\frac{dC}{C}\right]. \quad (2)$$

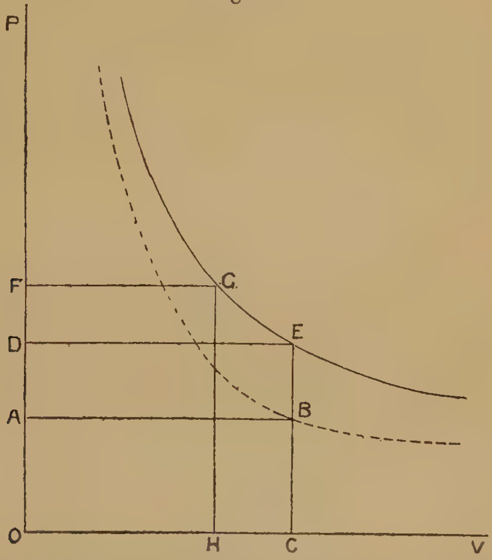
In the above deduction use has been made (as in all similar arguments) of a semipermeable partition, and it is important to consider exactly what character must be attributed to this. It seems to me that, on the one hand, it is impossible to assume impermeability for the metallic ions alone, since then it would be possible to allow the acid radical to diffuse through the partition, and leave behind a solution containing more positive than negative ions; a state of things which, according to all our experimental knowledge, cannot exist. On the other hand, if the partition is impermeable for both ions, it must be (at least effectively) impermeable for the undissociated salt too, since, if some of the salt were to diffuse out, the ions remaining in the solution would no longer be in equilibrium with the undissociated salt remaining, and some of the ions would combine: thus (effectively) ions as well as salt would have diffused out of the solution. I have therefore assumed a partition permeable only to water, but not to the salt or its ions. From this follows the important conclusion that the electromotive force depends not on the osmotic pressure of the metallic ions only, but on that of the solution as a whole.

(ii.) *Graphical Representation.*

Equation (2) becomes, of course, identical with (1) if the dissociation be complete, *i. e.* if γ be put $=1$. It is, however, in any case capable of graphic representation in an interesting manner.

In fig. 1, showing relations between dilution (V) and osmotic pressure (P), let the dotted curve be the rectangular hyperbola representing (at constant temperature) the behaviour

Fig. 1.



of a substance which obeys Boyle's law and does not dissociate; while the full curve represents the behaviour of the actual (dissociating) substance, which, however, is also assumed to obey Boyle's law. Then a rectangle under the dotted curve, such as OABC, will have the area

$$PV=RT.$$

A similar rectangle ODEC under the full curve has the area

$$PV=RT\{1+(n-1)\gamma\}=RT\iota,$$

since the pressure of the dissociating substance is greater in the ratio $1+(n-1)\gamma$, or as it may be more briefly written ι (van't Hoff's factor). If another point G be taken on the full curve and the rectangle OFGH drawn, its area will represent the value of RTι corresponding to the dilution OH: the difference between the two areas (using the suffixes 1 and 2 as previously) is

$$\mathrm{RT}(\iota_2-\iota_1)=\mathrm{RT}(n-1)(\gamma_2-\gamma_1).$$

But the area under the curve GHCE represents the value of

$$\int \mathrm{P}d\mathrm{V}=\mathrm{RT}\int \iota d\mathrm{V}=\mathrm{RT}\int\frac{\iota d\mathrm{C}}{\mathrm{C}}.$$

Hence to get a graphical representation of the electromotive force we must add to GHCE the rectangle OFGH and subtract ODEC, leaving the figure FGED. The latter, however, stands for the expression $\int \mathrm{V}\,d\mathrm{P}$; and we therefore arrive at the remarkable result that the *electromotive force is not proportional to the work of expansion* $\int \mathrm{P}\,d\mathrm{V}$ but to the converse integral, being exactly

$$\mathrm{E}=\frac{1-x}{r\epsilon}\int_{\mathrm{P}_1}^{\mathrm{P}_2}\mathrm{V}\,d\mathrm{P}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(iii.) *Solutions deviating from Boyle's Law.*

The above is the argument as it first occurred to me: but it will be found that the results arrived at are independent of one of the assumptions made, viz., that the osmotic pressure is proportional to the concentration. If we do not assume that, but, retaining the previous notation, write

$$\mathrm{P}=\mathrm{RT}\iota\mathrm{C},$$

where ι is now a factor no longer identical with $1+(n-1)\gamma$, but such as to take into account the deviations from Boyle's law as well, the deduction by means of the cyclic process will still be true, yielding equation (2) in the form

$$\mathrm{E}=\frac{\mathrm{RT}(1-x)}{r\epsilon}\left[\iota_2-\iota_1+\int_{\mathrm{C}_1}^{\mathrm{C}_2}\frac{\iota d\mathrm{C}}{\mathrm{C}}\right], \quad . \quad . \quad . \quad (4)$$

which in turn gives the same graphic result as before—that expressed by equation (3).

Now with regard to the deviations from Boyle's law, the most natural assumption one can make is that the osmotic pressure changes roughly in the manner indicated by van der Waals's equation, *i. e.* as the pressure is increased the volume (dilution) tends towards a limiting finite value, rather than towards zero. The effect of this difference is important: if the electromotive force of a concentration-cell be proportional to $\int P\,dV$, its value as calculated from van der Waals's equation might not differ sensibly from that calculated according to Boyle: indeed, if we put

$$P=\frac{RT\iota}{V-b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(neglecting the surface-tension term in the gaseous equation), we obtain a rectangular hyperbola parallel to the original one and the value of $\int P\,dV$ is strictly unchanged. But if the electromotive force depends on $\int V\,dP$, the case is different: as may easily be seen by reference to the diagram, the area between the curve and its vertical asymptote is increased by a rectangular portion whose area is simply proportional to the difference of pressure between the limits of the integral.

(iv.) *The Electrolytic Solution Pressure.*

Now Nernst's representation of the electromotive force between a metal and solution by means of the electrolytic solution pressure of the metal consists essentially in finding what value of P must be taken as the upper limit of the integral in order that, with the osmotic pressure of the solution for lower limit, its value may correspond to the observed electromotive force. In order to accomplish this with E proportional to $\int P\,dV$ (and assuming Boyle's law to $\log\frac{P_2}{P_1}$) it is necessary to take for the value of P at the upper limit

$$\Pi=10^{19} \text{ atmospheres}$$

nearly in the case of zinc. But for $\int V\,dP$, assuming that Boyle's law does not hold, we might still make use of the conception of the solution-pressure, and obtain quite a moderate value for it. The actual form of the equation is not essential to the argument; but assuming the form already given,

$$P=\frac{RT\iota}{V-b},$$

we may form a rough estimate as follows:—

Take the case of zinc in zinc-chloride solution: dissociation may practically be neglected, for in the most saturated solutions it is already very small. $1-x$ may be put equal to unity (in

Nernst's theory this is the case, the expression only entering into the electromotive force of a concentration-cell on account of the potential-difference between the two solutions). Then

$$\mathrm{E}r\epsilon = \int_{\mathrm{P}_1}^{\Pi} \mathrm{V}\,d\mathrm{P} = \mathrm{RT}\log\frac{\Pi}{\mathrm{P}_1} + b(\Pi - \mathrm{P}).$$

For $\mathrm{P}_1 = 22$ atmospheres (normal solution) $\mathrm{E} = 0{\cdot}5$ volt, whence the left-hand side is

$$0{\cdot}5 \times 2 \times 96540 \text{ joules} = 9{\cdot}654 \times 10^{11} \text{ ergs};$$

RT is about $2{\cdot}4 \times 10^{10}$ ergs at ordinary temperatures, and for b we will simply assume the volume of a gram-molecule of zinc chloride in the solid state $=46$ c.c. nearly. It follows that Π is about 20,000 atmospheres, a not impossible value. For the most alkaline metals it might be three or four times as great.

The above calculation is of course very uncertain, both on account of the form of equation assumed and the values of the numerical constants: it is intended only to give the order of magnitude of the solution-pressure, and for this it may serve. Whether there is any real meaning attached to the solution-pressure and to the process (common to Nernst's theory and the above) of extrapolating the electromotive force of a concentration-cell into regions of unattainable concentration, is a question to which I will not offer an answer. The reasoning may be taken merely as showing how to avoid the extravagantly high pressures usually quoted.

(v.) *Osmotic Pressure of Concentrated Solutions.*

Returning to the question of concentration-cells and the actually measurable phenomena they exhibit, it would appear that the chief use of electromotive measurements at the present time may be to determine the osmotic pressure of solutions of salts. The concentration attainable in salt solutions is such as to make it practically certain that large deviations from Boyle's law occur. This alone would of course render the usual logarithmic formula largely incorrect; it would have the same effect on the formula (2) developed above for the electromotive force of concentration-cells. But if that formula is correctly deduced from the assumptions made, a comparison between the values derived from it and the observed electromotive forces will afford a measure of how far the osmotic pressure deviates from that indicated by Boyle's law.

Experiments have therefore been undertaken in order to carry out this comparison. But in the equation to be used, another quantity occurs which is open to great uncertainty: this is the transference ratio x. It is well known that for concentrated solutions the value of x departs very considerably from the fixed value it possesses in dilute solutions, and as both measurement of it is difficult and the interpretation of the measurements is dubious, it is highly desirable to avoid it if possible. The way to do so was long ago shown by Helmholtz, and carried into practice by him and by Moser. It consists in breaking up the concentration-cell and interposing a pair of similar "non-polarizable" electrodes. Thus whilst in the cell

$$\mathrm{Zn : ZnSO_4\ (dil.) : ZnSO_4\ (conc.) : Zn}$$

migration of the ions occurs, in the couple

$$\mathrm{Zn : ZnSO_4\ (dil.) : Hg_2SO_4 : Hg : Hg : Hg_2SO_4 : ZnSO_4\ (conc.) : Zn}$$

it is avoided. Consideration of a thermodynamic cycle applicable to the latter, but otherwise similar to that described in § i., shows that the electromotive force of the couple is equal to that of the simple concentration-cell divided by $1-x$, or

$$E = \frac{RT}{r\epsilon}\left[(n-1)(\gamma_2-\gamma_1) + \int_{C_1}^{C_2}\{1+(n-1)\gamma\}\frac{dC}{C}\right] . \quad . \qquad (6)$$

In the tables given below are values calculated from this formula by means of Kohlrausch's tables of conductivity, and the values of γ deduced from them: they involve, of course the assumption that the degree of dissociation γ is really that calculated from the molecular conductivity. This assumption is possibly not quite correct, but it is certainly the best we can at present make.

(vi.) *Previous Measurements.*

A considerable number of experiments on concentration-cells have been published, but only a part of these are available to throw light on the questions considered in this paper. The most trustworthy measurements appear to be those of Helmholtz [*], made in connexion with the theory already referred to; Wright and Thomson [†], Moser [‡], Lussana [§], and Goodwin [||]. Each of these writers, unfortunately, expresses the concentration of his solutions differently, making a comparison between their results somewhat difficult. I have, however, chosen all the recorded observations on two salts, zinc sulphate and zinc chloride, and reduced them to a common reckoning by the aid of Kohlrausch's tables, and supplemented them by fresh experiments. The work of the writers named was mostly on concentration-cells of the usual type, involving migration of ions: it is consequently not directly available for determination of osmotic pressure; nor at present indirectly, since the information available on the transference ratios for these two salts is exceedingly scanty. Such as it is, it goes to confirm the relation indicated by a comparison of equations (2) and (6). On looking through the experimental material, however, a preliminary point attracted attention. Wright and Thomson made measurements with cells provided with electrodes of amalgamated zinc, electroplated zinc, and bright polished zinc; and they found that the electromotive force of a concentration-cell made with the same solutions differed according to the nature of the metal. If this be true, it implies a serious omission in all the theories of the subject that have hitherto been proposed, for however the electromotive force (or solution-pressure) of an electrode may vary with its physical state, if only the two electrodes are alike this variation is eliminated, according to the osmotic theories. The difference found amounted to as much as one third of the total E.M.F. of the concentration-cell: the amalgamated electrodes giving the largest, the polished ones the smallest values; and similar results were found for copper and cadmium. Notwithstanding this, and the carefulness of Wright and Thomson's work, I am inclined to think that they must have been deceived in the matter, on account of the difficulty in getting concordant results with electrodes that are not amalgamated. I made a test experiment with the materials I had to hand by the method described below, and found negative results as shown in the following table. Cells of the type

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[*] *Berl. Monatsber.* 1877, pp. 713–726; *Berl. Sitzber.* 1882, pp. 22–39, 825–836.

[†] Phil. Mag. [5] xvii. pp. 282–301, 377–391 (1884).

[‡] Wied. *Ann.* xiv. pp. 62–85 (1881); *Wien. Ber.* xcii. pp. 652–656 (1886)

[§] *Ist. Venet.* [7] iii. pp. 1111–1148 (1892).

[||] *Zeits. f. phys. Chem.* xiii. p. 577 (1894).

$$Zn : ZnSO_4 : Hg_2SO_4 : Hg$$

were set up with (α) amalgamated zinc rods, (β) zinc amalgam containing less than 1 per cent. of zinc, and their differences taken.

Concentration of $ZnSO_4$ (gm.-equiv./litre.)	E.M.F. in volt (a) − (β).
$3\sqrt{3}$	0·0061
3	64
$\sqrt{3}$	54
1	69
$\frac{1}{2}$	77
$\frac{1}{8}$	65

It will be seen that the irregularities observed are merely errors of experiment, and give no support to Wright and Thomson's opinion.

The previous experiments, reduced, are as follows :—

Zinc Chloride.

Concentration-cells with migration.

Moser's observations.

Gms. $ZnCl_2$ to 100 g. water.	E.M.F. in Daniells.	gm.-equiv./litre. 1000 C.	log C $= -\psi$.	E.M.F. from normal soln. Volts × 10^{-4}.	
1	...	0·1480	$\bar{4}$·17042	− 351	
3	0·0181	0·4389	$\bar{4}$·64241	156	
5	269	0·7306	$\bar{4}$·86367	60	
10	390	1·449	$\bar{3}$·16092	+ 70	Daniell taken as 1·08 volt. By interpolation normal solution lies 0·0060 volt above 5°/$_0$ solution.
15	470	2·149	$\bar{3}$·33219	157	
20	525	2·833	$\bar{3}$·45218	216	
25	587	3·493	$\bar{3}$·54311	283	
50	832	6·554	$\bar{3}$·81650	547	
75	1100	9·213	$\bar{3}$·96442	837	
100	1347	11·52	$\bar{2}$·06145	1104	
125	1626	13·60	$\bar{2}$·13345	1405	
150	1932	15·37	$\bar{2}$·18667	1735	

Wright and Thomson's observations.

nZnCl$_2$+ 100H$_2$O.	E.M.F. in B.A. volts.	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. from normal soln. Volts $\times 10^{-4}$.	
$n=$ 0·172	0·2590	0·1909	$\bar{4}$·28076	− 233	B.A. volt taken as 0·9867 volt. By interpolation normal solution lies 0·0040 volt above 0·754 solution. * extrapolated.
0·25	0·2541	0·2775	$\bar{4}$·44330	184	
0·754	0·2397	0·8340	$\bar{4}$·92115	40	
2·04	0·2181	2·211	$\bar{3}$·34460	+ 176	
3·3	0·2071	3·412	$\bar{3}$·53296	286	
6·1	0·1863	6·115	$\bar{3}$·78639	494	
9·8	0·1120	9·132	$\bar{3}$·96056	1237	
24·4	...	17·58*	$\bar{2}$·24511	2357	

Concentration-cells without migration.

Helmholtz's observation.

Mass of water to 1 g. ZnCl$_2$.	E.M.F. in calomel cells.	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. in volts $\times 10^{-4}$.	
9·1992	...	1·574	$\bar{3}$·19700	...	Calomel cell taken by Helmholtz at 1·043 volts on the assumption that the Siemens unit $=0·9717^{\omega}$. But it is really $=0·9407^{\omega}$.
0·8	0·11541	13·60	$\bar{2}$·13354	1165·4	

Moser's observation.

	E.M.F. in Daniells.	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. in volts $\times 10^{-4}$.	
ZnCl$_2$+ 750H$_2$O.	...	0·1495	$\bar{4}$·17464	...	
ZnCl$_2$+ 100H$_2$O.	0·0516	1·102	$\bar{3}$·04222	557	

Goodwin's observations.

gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. Volts $\times 10^{-4}$.	
0·2 to 0·02	$\bar{4}$·301 to $\bar{5}$·301	777	Partly with Hg$_2$Cl$_2$; partly with AgCl as depolarisator.
0·1 to 0·01	$\bar{4}$·000 to $\bar{5}$·000	790	
0·02 to 0·002	$\bar{5}$·301 to $\bar{6}$·301	843	
0·01 to 0·001	$\bar{5}$·000 to $\bar{6}$·000	854	

ZINC SULPHATE.

Concentration-cells with migration.

Moser's observations.

Mass of $ZnSO_4 \cdot 7H_2O$ to 100 g. soln.	E.M.F. in Daniells.	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. from normal soln. Volts × 10^{-4}.	
1	...	0·0731	$\bar{5}$·8639	−185	By interpolation normal solution lies 0·0010 volt below 15°/₀ solution.
15	0·018	1·155	$\bar{3}$·0626	+ 10	
30	0·0225	2·496	$\bar{3}$·3972	59	
45	0·0295	4·099	$\bar{3}$·6127	134	
60	0·0382	6·44	$\bar{3}$·8089	228	

Wright and Thomson's observations.

$nZnSO_4+100H_2O$.	E.M.F. in B.A. volts.	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. from normal soln. Volts × 10^{-4}.	
n=0·100	0·0395	0·116	$\bar{4}$·0645	−153	
0·167	372	0·192	$\bar{4}$·2838	130	
0·237	348	0·271	$\bar{4}$·4326	106	By interpolation normal solution lies 0·0008 volt below $ZnSO_4+100H_2O$.
0·5	284	0·548	$\bar{4}$·7388	43	
1·0	232	1·115	$\bar{3}$·0472	+ 8	
2	169	2·359	$\bar{3}$·3727	70	
3	118	3·272	$\bar{3}$·51 8	120	
4	056	4·341	$\bar{3}$·6376	182	
5	...	5·321	$\bar{3}$·7260	237	

Lussana's observations.

Mols. $ZnSO_4$ in 100,000 g. water.	E.M.F. volts (differences)	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. from normal soln. Volts × 10^{-4}.	
12·0	> 0·0052	0·110	$\bar{4}$·0414	−166	By interpolation normal solution lies 0·0031 volt below 72·7 $ZnSO_4$ solution. Temperature about 23°.
18·8	> 83	0·149	$\bar{4}$·1732	114	
72·7	> 80	0·724	$\bar{4}$·8597	31	
195·8	> 114	1·791	$\bar{3}$·2531	+ 49	
556·3		4·150	$\bar{3}$·6180	163	

Concentration-cells without migration.

Moser's observations.

	E.M.F. in Daniells.	gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. in volts $\times 10^{-4}$
$ZnSO_4+800H_2O$.	...	0·146	$\bar{4}$·1644	...
$ZnSO_4+100H_2O$.	0·0227	1·126	$\bar{3}$·0515	245

Goodwin's observations.

gm.-equiv./litre. 1000 C.	log C $=-\phi$.	E.M.F. in volts $\times 10^{-4}$.	
0·2 to 0·02	$\bar{4}$·301 to $\bar{5}$·301	427	With $PbSO_4$ as depolarisator.
0·1 to 0·01	$\bar{4}$·000 to $\bar{5}$·000	440	
0·02 to 0·002	$\bar{5}$·301 to $\bar{6}$·301	522	

(vii.) *New Experiments.*

To test the accuracy of the relation between electromotive force and osmotic pressure as given in the foregoing theoretical treatment, and to provide data for calculating the osmotic pressure, it is clearly necessary to make more systematic and complete experiments than has so far been done. In endeavouring to fill up this deficiency, I chose in the first place the salts of zinc, because zinc electrodes are well known to give results of a satisfactory degree of constancy. The measurements so far made have been on the chloride and sulphate of zinc: the former possesses the advantage of an exceptionally great solubility, allowing of investigations in the regions of concentration which are especially interesting from the point of view of this paper. The sulphate is, however, preferable in the matter of purity, and neutrality; whilst as the course of the molecular conductivity curve is considerably different for the two salts, a comparison of results will give some indications as to the properties common to salts in general.

Materials.—For electrodes, zinc rod (obtained from Johnson and Matthey) was cleaned with emery-cloth, and amalgamated: or when liquid electrodes were to be used, some of the same zinc was dissolved by gentle heating in about 100 times its weight of mercury. The zinc rods on standing for days in a zinc solution sometimes became coated with a flocculent black deposit, the nature of which was not determined with certainty, but was probably metallic indium. The deposit appeared to make no difference to the electromotive force, and after repeated cleaning of the rods gradually ceased.

The zinc sulphate contained no iron, or other appreciable impurity; solutions were made up from it, as obtained, and merely filtered into stock bottles. Several strong solutions were weighed out direct: those below normal strength were made by diluting a strong solution with pipette and measure-flask.

The zinc chloride, in the form of fused sticks, contained no appreciable impurity except zinc hydroxide: a strong solution of the chloride was found to dissolve an appreciable amount of the hydroxide, which is precipitated on dilution. To obtain a neutral solution the sticks were dissolved in water and hydrochloric acid added till the liquid just began to turn litmus red: the density was taken, and the concentration calculated from the tables in Kohlrausch and Holborn's *Leitvermögen der Elektrolyte*: weaker solutions could be prepared by dilution, without further inconvenience.

The mercurous sulphate (Harrington's) was that used for Clark cells; it remained perfectly white in use. The mercurous chloride at first contained traces of mercuric chloride, but on washing proved quite satisfactory.

Cells.—The cells used are here referred to for brevity as "mercury" and "concentration" cells. The former are of the types,

$$Zn : ZnCl_2 : Hg_2Cl_2 : Hg,$$

$$Zn : ZnSO_4 : Hg_2SO_4 : Hg,$$

the latter

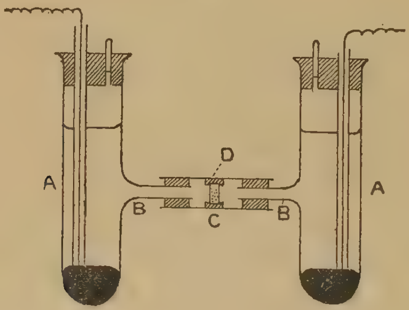
$$Zn : ZnCl_2 \text{ (dilute)} : ZnCl_2 \text{ (conc.)} : Zn,$$

$$Zn : ZnSO_4 \text{ (dilute)} : ZnSO_4 \text{ (conc.)} : Zn.$$

The "mercury" cells were of two kinds, "rod" and "amalgam." The rod cells were made up in short wide test-tubes, closed by corks with two borings: one of these held in place the glass tube through the end of which a platinum wire was sealed for communication with the mercury: when the mercury had been poured in and the platinum fixed in place, the depolarisator and the solution were added through the other boring, and lastly the zinc rod fixed in it: the platinum wire consequently remained clean and dry. The amalgam cells were made up in H form, with similar precautions.

After a good many failures a form of "concentration" cell was designed which satisfied the requirements of facility of setting up and cleaning, freedom from diffusion, and low internal resistance: it served equally for rod or amalgam electrodes. A pair of glass tubes, A A fig. 2 (8 cm. × 2), have each a short side tube, B B, blown on at about half their length: the side tubes fit by means of short pieces of rubber tubing inside a straight tube C (3 cm. × 1) which carries the porous diaphragm; this is a fragment of a porous soup-plate D, filed round and fitted in by a ring of india-rubber. Each tube A is closed by a rubber stopper with two holes, one for the electrode; the other, made merely for convenience in filling, is eventually closed by a glass rod. By working the side tube B backwards and forwards in the central tube C, the air can be driven out of the latter.

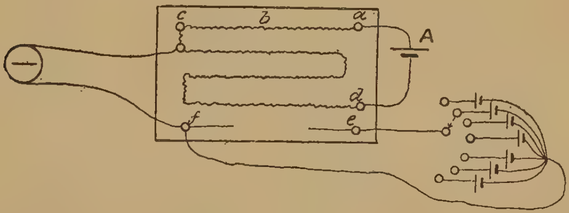
Fig. 2.



The cells were placed—up to six at a time—in a wooden holder by which they were held in a sink filled with water; the sink was provided with a thermoregulator, and kept within one or two tenths of 20°·2 cent. The Clark cells were kept in the same thermostat.

Electrical measuring arrangements.—The E.M.F. of the concentration-cells, or in the case of the "mercury" cells the difference between their E.M.F.'s or between each one and a Clark, was measured by the compensation method. At first a Crompton potentiometer was used, but subsequently given up on account of the necessity for frequently readjusting; a P.O. box was then adopted, the resistance being always kept greater than 100 ohms. Under these circumstances the accumulator (charged fortnightly, and discharged for half an hour at maximum rate before using) gave such a constant E.M.F. that it was only necessary to take a reading with the Clark cell once a day to standardize. The connexions are shown in fig. 3. The accumulator A was connected to the terminals of the box *a d*: 1000 ohms taken out of the arm *b c*, and about 430 from *c d*, making the E.M.F. between *b* and *c* equal to that of a Clark cell. The Clark or other cell was connected by a multiple switch from the tapping-key at *e* through a Crompton "midget" galvanometer to *c*, the wire touching on the way at the other tapping-key *f*; putting down the latter short-circuits the galvanometer and damps it, while the right-hand key puts the experimental cell in circuit. The E.M.F. between *a* and *d* having first been found when the Clark is in circuit, may be regarded as known for the subsequent experiments; for although the total resistance between *a* and *d* varies, it is always so large as to leave the E.M.F. between the terminals of the accumulator practically unaffected.

Fig. 3.



The results obtained are shown in the following tables and also on the accompanying diagram (p. 598):—

ZINC CHLORIDE.

1st *Series.*—Solution (x) prepared as described above. Density 1·1238 at 19°·7 (referred to water at 4°): corresponding concentration calculated to be 2·19 times normal. Amalgam cells.

gm.-equiv./litre (1000 C).	log C = $-\psi$.	E.M.F. observed. Volts.	E.M.F. differences. Volts × 10^{-4}.	E.M.F. from normal. Volts × 10^{-4}.
x=2·19	$\bar{3}$·340	1·0406		+249
x/2	$\bar{3}$·039		> 220	+ 29
x/4	$\bar{4}$·738		> 225	−196
x/8	$\bar{4}$·437		> 230	−426
x/16	$\bar{4}$·136		> 228	−654
x/32	$\bar{5}$·835		> 215	−869

2nd *Series.*—Solution (y). Density 1·6049 at 20°·3: concentration 12·33 normal. Amalgam cells.

gm.-equiv./litre (1000 C).	log C = $-\psi$.	E.M.F. observed. Volts.	E.M.F. from normal. Volts × 10^{-4}.
y=12·33	$\bar{2}$·091	0·9378	+1263
y/10	$\bar{3}$·091	1·0573	+ 68
y/100	$\bar{4}$·091	1·1298	− 657

3rd *Series.*—Solution (y) as before. Amalgam cells.

gm.-equiv./litre (1000 C).	log C = $-\psi$.	E.M.F. observed. Volts.	E.M.F. from normal. Volts × 10^{-4}.
y=12·33	$\bar{2}$·091	0·9382	+1288
y/2	$\bar{3}$·790	1·0005	+ 665
y/4	$\bar{3}$·489	1·0300	+ 370
y/8	$\bar{3}$·188	1·0528	+ 142
y/16	$\bar{4}$ 887	1·0755	− 85
y/80	$\bar{4}$·188	1·1269	− 599

4th *Series.*—Solution (z). Density 1·9538 at 20°. Since this density lies beyond the range of the tables, another was prepared from it, by mixing 40 c.c. of (z) with 20 c.c. of water. The density of the latter (2/3 z) was 1·6624 at 20°: whence the concentration (from the tables) = 13·51 normal, and thence that of the original solution is 19·94 normal. The solution (2/3 z) was diluted similarly to form (4/9 z): density of the latter 1·4536 at 20°, whence concentration 9·089 normal: it was then diluted to (4/90 z) with pipette and flask in the usual way. Amalgam cells.

Solution.	log C = $-\psi$.	E.M.F. observed. Volts.	E.M.F. from normal. Volts × 10^{-4}.
z	$\bar{1}{\cdot}000$	0·8539	+2113
2/3 z	$\bar{2}{\cdot}131$	0·9246	+1406
4/9 z	$\bar{3}{\cdot}958$	0·9740	+ 912
4/90 z	$\bar{4}{\cdot}958$	1·0683	− 31

Mean electromotive force of a cell containing equivalent normal ZnCl$_2$ solution and 1 per cent. zinc amalgam (from the four series) = 1·0654 volts.

Concentration-cells (with migration).

Solutions.	log C = $-\psi$.	E.M.F. Volts × 10^{-4}.
y : $y/10$	$\bar{2}{\cdot}091$: $\bar{3}{\cdot}091$	1309
$y/10$: $y/100$	$\bar{3}{\cdot}091$: $\bar{4}{\cdot}091$	427

ZINC SULPHATE.

1*st Series.*—Twice normal solution and its dilutions. Rod cells.

gm.-equiv./litre. 1000 C.	log C = $-\psi$.	E.M.F. observed. Volts.	E.M.F. differences. Volts × 10^{-4}.	E.M.F. normal. Volts × 10^{-4}.
2	$\bar{3}{\cdot}301$	1·4558	> 183	+ 78
2/5	$\bar{4}{\cdot}602$	...	> 191	−105
2/25	$\bar{5}{\cdot}903$	...		−296

2*nd Series.*—Twice normal solution and its dilutions. Rod cells.

gm.-equiv./litre. 1000 C.	log C = $-\psi$.	E.M.F. differences. Volts × 10^{-4}.	E.M.F. from normal. Volts × 10^{-4}.
2	$\bar{3}{\cdot}301$	> 85	+ 85
1	$\bar{3}{\cdot}000$	> 80	0
1/2	$\bar{4}{\cdot}699$	> 79	− 80
1/4	$\bar{4}{\cdot}398$	> 77	−159
1/8	$\bar{4}{\cdot}097$		−236

3rd Series.—Solutions made up directly by weight. Rod cells.

gm. equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. Volts.	E.M.F. differences. Volts × 10^{-4}.	E.M.F. from normal. Volts × 10^{-4}.
(Clark)	$\bar{3}{\cdot}800$ nearly	(1·4285 assumed.)		+355
$3\sqrt{3}$	$\bar{3}{\cdot}715$	...	> 81	+274
3	$\bar{3}{\cdot}477$	...	> 132	+142
2	$\bar{3}{\cdot}301$	...	> 60	+ 82
$\sqrt{3}$	$\bar{3}{\cdot}239$	...	> 23	+ 59

4th Series.—Solutions made up directly by weight. Amalgam cells.

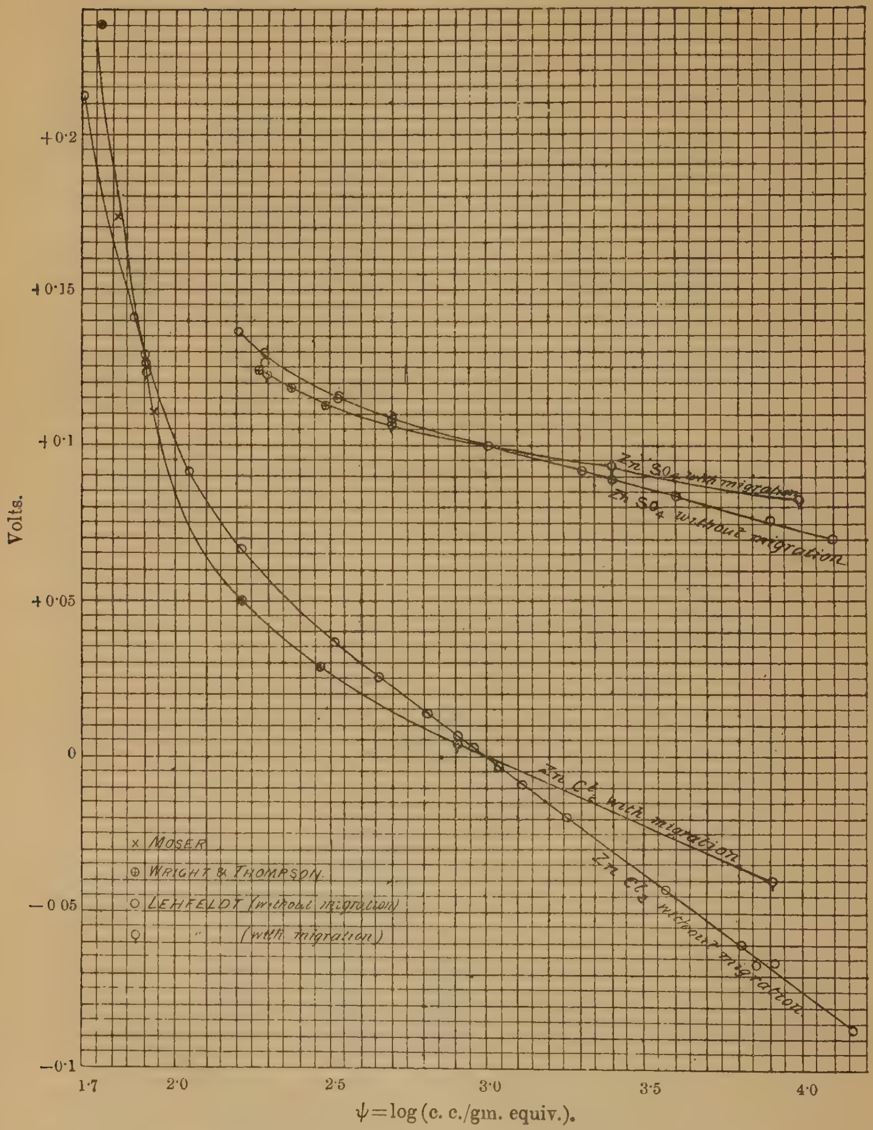
gm.-equiv./litre. 1000 C.	log C $=-\psi$.	E.M.F. Volts.	E.M.F. from normal. Volts × 10^{-4}.
$3\sqrt{3}$	$\bar{3}{\cdot}715$	1·4306	+296
3	$\bar{3}{\cdot}477$	1·4452	+150
2	$\bar{3}{\cdot}301$	1·4520	+ 82
$\sqrt{3}$	$\bar{3}{\cdot}239$	1·4545	+ 57

Concentration Cells.

Solution.	log C $=-\psi$.	E.M.F. Volts × 10^{-4}.
$3\sqrt{3}$: 2	$\bar{3}{\cdot}715$: $\bar{3}{\cdot}301$	162
2 : 2/5	$\bar{3}{\cdot}301$: $\bar{4}{\cdot}602$	131
2/5 : 2/25	$\bar{4}{\cdot}602$: $\bar{5}{\cdot}903$	111
$\sqrt{3}$: 1	$\bar{3}{\cdot}239$: $\bar{3}{\cdot}000$	47
1 : 2/5	$\bar{3}{\cdot}000$: $\bar{4}{\cdot}602$	66
1 : 1/10	$\bar{3}{\cdot}000$: $\bar{4}{\cdot}000$	178
1 : 1/100	$\bar{3}{\cdot}000$: $\bar{5}{\cdot}000$	307

Electromotive Force of Concentration Cells (without migration) *at* 20°.

gm.-eq./litre (1000 C).	log C = −ψ.	E.M.F. from normal solution. Volts ×10−4.			*i* from conductivity.
		Obs. (read off curve).	Calc. by equation (2).	Calc. (Nernst).	
Zinc Chloride.					
0·001	$\bar{6}$·000	...	2108	2363	2·888
2	·301	...	1861	2108	2·852
5	·699	...	1544	1776	2·782
0·01	$\bar{5}$·000	−1537	1310	1525	2·728
2	·301	1301	1083	1278	2·658
3	·477	1158	956	1137	2·604
5	·699	976	795	961	2·534
0·1	$\bar{4}$·000	747	588	720	2·446
2	·301	526	392	487	2·340
3	·477	392	286	359	2·252
5	·699	229	158	199	2·146
1	$\bar{3}$·000	0	0	0	1·970
2	·301	+ 219	...	...	1·706
3	·477	365	...	...	1·530
4	·602	465	...	...	1·406
5	·699	556	...	...	1·336
7	·845	734	...	...	1·220
10	$\bar{2}$·000	1016	...	...	1·128
15	·176	1580	...	...	..
20	·301	2116	...	...	...
Zinc Sulphate.					
0·001	$\bar{6}$·000	...	−1250	−1417	1·841
2	·301	...	1098	1258	1·788
5	·699	...	906	1055	1·701
0·01	$\bar{5}$·000	− 743	770	908	1·627
2	·301	617	639	763	1·554
3	·477	467	567	683	1·509
5	·699	369	477	581	1·457
0·1	$\bar{4}$·000	272	361	442	1·395
2	·301	190	247	302	1·343
3	·477	141	182	222	1·315
5	·699	80	104	126	1·276
1	$\bar{3}$·000	0	0	0	1·227
2	·301	+ 82	...	...	1·172
3	·477	146	...	...	1·133
4	·602	225	...	...	1·102
5	·699	293	...	...	1·077
6	·778	356	...	...	...



The general character of the results arrived at is clearly indicated by the diagram. Considering, first, the case of zinc chloride, and starting from the lower end of the curve, representing the most dilute solutions, the relation should, for indefinitely great dilution, be that given by Nernst's equation,

$$E = \frac{3RT}{2\epsilon} \log_e \frac{C_2}{C_1} = 2{\cdot}3026 \times \frac{3}{2} \frac{RT}{\epsilon} (\psi_1 - \psi_2);$$

i. e., graphically a straight line with a slope $\frac{dE}{d\psi} = 87$ millivolts for unit difference in the common logarithm. Since, however, the dissociation of the salt is sensibly incomplete even for very dilute solutions, the straight part of the curve does not come within the range of experiment ; the electromotive differences are those calculated from equation (2) above, and given in table. These are : from $\frac{1}{10000}$ normal ($\psi=7$) to $\frac{1}{1000}$ normal ($\psi=6$) 84 millivolts, from milli- to centi-normal ($\psi=6$ to $\psi=5$) 80 millivolts, from centi- to deci-normal ($\psi=5$ to $\psi=4$) 72 millivolts, the curve consequently being convex upwards. The experimental results agree satisfactorily with the calculated over the range centi- to deci-normal, showing—as might be expected—that the deviation from the value given by the logarithmic formula is accounted for by the incomplete dissociation of the salt, and does not imply any departure from Boyle's law as applied to the solution.

Goodwin's observations made over the range from $\psi=\bar{6}$ to $\psi=\bar{4}{\cdot}3$, which, to save space, are not shown on the diagram, follow satisfactorily on my own, extending the curve into regions of greater dilution. Goodwin compared his observations with the results of the formula (due to Nernst)

$$E = \frac{RT}{r\epsilon} \log \frac{\gamma_2 C_2}{\gamma_1 C_1},$$

where γ is the degree of dissociation. This formula is contrary to that arrived at thermodynamically above, and I think is wrong. Unfortunately there is no means of deciding between them, since for great dilution they give values not far apart, and the experimental numbers lie between, while for strong solutions both formulæ are vitiated by the inapplicability of Boyle's law. It may be noted, however, that strong solutions of $ZnSO_4$ and $ZnCl_2$ show a maximum of conductivity (and so presumably of ionic concentration), and thus Nernst's formula would make the concentrated solution *anodic* to the dilute, which is not the case. Beyond this point, however, the curve, which on account of incomplete dissociation should continue to bend downwards, is found instead to pass through a point of inflexion and then bend quite sharply upwards, indicating that the effect of departure from the gaseous laws greatly prevails over that of incomplete dissociation. Thus the values calculated for the range decinormal ($\psi=4$) to normal ($\psi=3$) and normal to ten times normal ($\psi=2$) on the assumption of Boyle's law are 59 and 34 millivolts respectively: the observed values are 75 and 102.

Instead of any distinguishable point of inflexion, the curve shows a long portion that is practically straight. In this region, then, the osmotic pressure may be calculated very simply. For then we may put

$$\mathrm{E}=-a\psi+b=-a\log_{10}\mathrm{V}+b,$$

whence

$$\frac{d\mathrm{E}}{d\psi}=-a,\quad \frac{d\mathrm{E}}{d\mathrm{V}}=-\frac{a}{\mathrm{V}\log_e 10}.$$

But from (3), for a cell without migration,

$$r\epsilon\mathrm{E}=\int\mathrm{V}d\mathrm{P},$$

whence

$$r\epsilon\frac{d\mathrm{E}}{d\mathrm{V}}=\mathrm{V}\frac{d\mathrm{P}}{d\mathrm{V}},$$

and

$$\frac{d\mathrm{P}}{d\mathrm{V}}=-r\epsilon\frac{a}{\mathrm{V}^2\log_e 10},$$

giving

$$\mathrm{P}=r\epsilon\frac{a}{\mathrm{V}\log_e 10}+\text{const.}\dots\quad . \quad . \quad (7)$$

The constant term is small, since the straight part of the curve extends into regions where the deviation from Boyle's law is negligible. It follows, therefore, that we may put approximately $\mathrm{P}=r\epsilon\frac{a}{\mathrm{V}\log_e 10}$, and regard the combined effect of varying dissociation and the finite concentration of the solution as simulating the behaviour of an ideal gas.

From the value 0·0747 volt for $\psi=4$ to $\psi=3$ we get

$$\frac{r\epsilon a}{\log_e 10}=\frac{193080\times 0\cdot 0747}{2\cdot 3026}=6264 \text{ joules}.$$

Now for an undissociated solution obeying Boyle's law we should have at 20°

$$PV = RT = 8{\cdot}316 \times 293 = 2437 \text{ joules};$$

the ratio is $$\frac{6264}{2437} = 2{\cdot}73.$$

But van't Hoff's factor as determined by means of the electrolytic conductivity is 2·45 for decinormal, 1·97 for normal solution: hence the osmotic pressure may be reckoned to exceed that calculated from the laws of gases by about 11 per cent. in the former case, 38 per cent. in the latter.

The curve for zinc sulphate shows the same general trend, but differs in certain respects. I could not obtain measurements with mercury cells of concentration much below decinormal. Goodwin met with the same difficulty, and attributed it to some secondary reaction of the Hg_2SO_4. I am inclined to think that it is mainly due to the appreciable solubility of that salt, which prevents it from constituting an ideal depolarizing electrode (see Goodwin's work on TiCl *loc. cit.*). In either case the difficulty remains; but if it be permissible to associate Goodwin's measurements with $PbSO_4$ as depolarisator with mine, as shown on the diagram, it will be found that the curve bends sharply down to the right, as it should do, since for limiting dilution the value of $\frac{dE}{d\psi}$ should be 0·058 volt for unit difference in common logarithm (2/3 of the value for the chloride, since there are only two ions); while in the straight part of the curve $\frac{dE}{d\psi}$ has the abnormally low value of 0·0272 volt. On account of this sharp curvature the integration constant in (7) cannot be neglected, and the approximate estimate of the osmotic pressure given in the preceding paragraph fails.

The few observations I have made with concentration-cells of the ordinary type were for the sake of verifying the previous work of Moser, Wright & Thomson, and Lussana. This they do satisfactorily; but I do not consider that, at present, the measurements are sufficiently exact to justify a calculation of Hittorf's transference ratios in this way. It may be seen from the curve that x increases for $ZnCl_2$ from about 0·6 in dilute solution to more than unity in strong solution, in agreement with the results of migration experiments; but before calculating the values in detail it will be necessary to extend the experimental data, and to take into theoretical account the successive (" stufenweise ") dissociation which undoubtedly occurs in this salt.

(viii.) *Calculation of the Osmotic Pressure.*

To calculate the osmotic pressure we have

$$r\epsilon E = \int V dP.$$

Hence

$$r\epsilon \frac{dE}{dV} = V \frac{dP}{dV},$$

$$P = r\epsilon \int \frac{1}{V} \frac{dE}{dV} dV.$$

The integral was evaluated graphically by the method described in the following "Note on Graphical Treatment," being first transformed, as there shown, into

$$P = r\epsilon [EC] - r\epsilon \int E\, dC,$$

where $C = 1/V$ is the concentration. It was assumed that for a centinormal solution the osmotic pressure might be calculated according to Boyle's law, from the concentration and the degree of dissociation as indicated by measurements of conductivity; *i. e.* $P = RT\iota C$. For $ZnCl_2$ we have $\iota = 2{\cdot}728$, for $ZnSO_4$ $\iota = 1{\cdot}627$ from Kohlrausch's data; C being 10^{-2} gm.-equiv./litre. Hence

$$P = 83157 \times 293 \times 2{\cdot}728 \times 10^{-2} = 0{\cdot}658 \text{ atmos}$$
$$(10^6 \text{ dynes/sq. cm.})$$

for zinc chloride, and

$$P = 83157 \times 293 \times 1{\cdot}627 \times 10^{-2} = 0{\cdot}396 \text{ atmo}$$

for zinc sulphate. The differences in pressure between centinormal and the more concentrated solutions were then measured by the planimeter, with the results shown in the following table:—

Zinc Chloride.

Gm.-equiv./litre.	Osmotic Pressure P (atmos).	PV.	$\frac{PV}{\iota}$.
0·01	0·658	65·8	24·12
0·1	6·63	66·3	27·1
1	63·7	63·7	32·3
2	123·6	61·8	37·1
3	193	64·3	42·0
4	270	67·5	
6	446	74·3	
8	660	82·5	
10	1006	100·6	
12	1475	122·9	
14	2029	144·8	
16	2670	166·9	
18	3396	188·5	
20	4207	210·3	

The numbers in the column PV show at first apparent irregularities; but I think these are not due to errors of experiment, but are real fluctuations due to the combined effect of the decreasing dissociation of the salt and the increasing departure from Boyle's law. This complication can be partly eliminated by taking the quotient $\frac{PV}{\iota}$ the ι being determined from the conductivity. Undoubtedly the values of van't Hoff's factor ι so arrived at are somewhat uncertain, but they are probably near enough to the truth to serve the immediate purpose of bringing out the character of the deviations from the gaseous laws. Assuming the values of ι to be correct, the quotients PV/ι should be constant so far as the gaseous laws are applicable. The table shows that even for a decinormal solution, with a pressure of 7 atmospheres the deviation is marked. It is about as great as that for sulphur dioxide or ammonia, but in the opposite direction.

Large deviation is, of course, to be expected on account of the large size of the dissolved molecules, if for no other reason.

It will be seen that there is a decided difference between the behaviour of the chloride and the sulphate. In the latter the values both of PV and PV/ι show a well-marked

Zinc Sulphate.

Gm.-equiv./litre.	Osmotic Pressure. P (atmos).	PV.	$\frac{PV}{i}$.
0·01	0·396	39·6	24·12
0·1	3·34	33·4	23·9
1	24·0	24·0	19·6
2	47·7	23·8	20·3
3	83·5	27·8	24·5
4	137	34·2	31·0
5	196	39·2	36·4
6	263	43·8	

minimum. The sulphate therefore follows the same rule as the ordinary gases, deviating first on the side of less elasticity than a perfect gas; afterwards, however, as the specific volume becomes very small, on the opposite side.

(ix.) *Summary.*

In the preceding pages an expression is obtained for the E.M.F. of a concentration-cell, with or without migration, by means of a thermodynamic cycle: the expression, which is applicable to strong as well as weak solutions, is given first, on the assumption of Boyle's law, in terms of the degree of dissociation of the salt as found from the electrical conductivity; afterwards, without that assumption, in more general terms. According to this expression the E.M.F. of a cell depends on the total osmotic pressure of the salt, not on that of the metallic ion only.

Experiments are then described, both old ones recalculated, and new ones made for the occasion, in which the E.M.F. of concentration-cells of $ZnCl_2$ and $ZnSO_4$ are measured; the results being expressed by curves and tables.

Finally, from the data thus provided the osmotic pressures of those salts in solutions nearly up to the point of saturation are calculated, and the analogy between those pressures and the pressures of highly compressed gases pointed out.

East London Technical College,
June 1900.

Discussion.

Mr. Whetham said there was one form of membrane which is quite permeable to water, and yet does not allow either salts or the ions to get through. He referred to the free surface of the solution itself. The water being volatile can get out, but the salt cannot.

Dr. Donnan said the author seemed to have discovered things well known; for instance, the integral $\int V dP$ is generally taken as proportional to E.M.F. He expressed his interest in the explanation of the difficulty in the logarithmic formula.

Dr. Lehfeldt, in reply, said Goodwin had used the integral $\int V dP$, but had not made any numerical calculations by means of it, or given any satisfactory proof of it.

XXXVII. *Note on the Graphical Treatment of Experimental Curves.* *By* R. A. Lehfeldt[*].

When as the result of experiments a relation between two quantities

$$y=f(x)$$

has been found, it is sometimes desirable to calculate from it some other function of x of a kind that involves differentiating y. The form of the function f being unknown, it is necessary to deal directly with the numerical observations, or with the curve expressing them. This is often done by finding an empirical equation for $y=f(x)$ and differentiating it, but to find a satisfactory empirical equation is not always possible; and if the subsequent treatment involves integration, the choice of forms is closely limited by the possibilities of the integration. There remains of course the method of differentiating the experimental curve graphically, by drawing tangents; but this should be avoided if it is in any way possible to do so, because the errors of the experimental curve are greatly exaggerated in taking its tangents; and no subsequent process of integration can smooth out the errors thus introduced.

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[*] Read November 9, 1900.

In certain cases the difficulty can be avoided, and a process of graphical integration, which can be satisfactorily performed, substituted for the graphical differentiation. Thus if it be required to obtain a quantity z such that

$$z = \int \phi(x) f'(x)\, dx,$$

where ϕ is a known function, integrate this expression by parts, giving

$$z = [\phi(x) f(x)] - \int \phi'(x) f(x)\, dx.$$

Here since $\phi(x)$ is known, $\phi'(x)$ can be calculated: the experimental values of $f(x)$ may then be multiplied by $\phi'(x)$, and the products plotted with respect to x as abscissa, and the curve so obtained integrated by a planimeter.

It will, however, often happen that $\phi'(x)f(x)$ is not suitable for accurate plotting. In this case the independent variable must be changed to $\phi(x) = w$, say. Then

$$\begin{aligned} z &= [\phi(x) f(x)] - \int \phi'(x) f(x)\, dx \\ &= [wy] - \int \phi'(x)\, y \frac{dx}{dw} \cdot dw \\ &= [wy] - \int y\, dw. \end{aligned}$$

Two examples that may occur in practice are

$$\phi(x) = \log x. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

Then

$$z = \int \log x \frac{dy}{dx} dx = [y \log x] - \int y\, d(\log x).$$

$$\phi(x) = \frac{1}{x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

Then

$$z = \int \frac{1}{x} \frac{dy}{dx} dx = \left[\frac{y}{x}\right] - \int y d\left(\frac{1}{x}\right).$$

The latter is the case occurring in the preceding paper "On Electromotive Force and Osmotic Pressure."

Another instance, which I did not see how to deal with at the time, occurs in my paper "On the Vapour-Pressure of Liquid Mixtures" (Phil. Mag. [5] xlvi. p. 61, 1898), where the relation

$$x\frac{d\log p_1}{dx}+(1-x)\frac{d\log p_2}{dx}=0$$

was to be verified: here x is the molecular fractional composition of a binary liquid mixture, p_1, p_2 the vapour-pressures of the two components. It is sometimes much easier to measure one of the vapour-pressures than the other. Suppose p_1 to be measured, then

$$\log p_2=-\int\frac{x}{1-x}\frac{d\log p_1}{dx}dx.$$

Hence

$$\log p_2=\left[\frac{-x}{1-x}\log p_1\right]+\int\frac{\log p_1}{(1-x)^2}dx,$$

and the numerical solution becomes practicable.

XXXVIII. *On a Phase-Turning Apparatus for use with Electrostatic Voltmeters. By* ALBERT CAMPBELL, *B.A.*[*]

[Abstract.]

ELECTROSTATIC voltmeters are particularly insensitive at the lower parts of their ranges, the divisions closing in very much towards the zero point. When measurements of small direct-current potential-differences have to be made it is an easy matter to add to the voltage to be measured a constant voltage large enough to bring the deflexion to an open part of the scale. If the small voltage to be measured is an alternating one it is necessary that that the auxiliary voltage should alternate with the same frequency and be in phase with it. The apparatus described enables the phase of the auxiliary voltage to be turned until it agrees with the one to be measured. The phase-difference referred to is not the time lag, but the angle whose cosine is the power-factor, and may be called the power lag. The method is to get two independent voltages, U_1 and U_2, differing in power phase by $\pi/2$ and to add together suitable fractions of these, such as $U_1 \sin \phi$, $U_2 \cos \phi$. The resultant is equal to U_1, but with the power phase turned through ϕ. The unknown small voltage is connected in series with an auxiliary voltage and a voltmeter, and the phase of the latter voltage is turned until the maximum deflexion is obtained.

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[*] Read November 9, 1900.

XXXIX. *On a Method of Measuring Power in Alternating Current Circuits.* *By* ALBERT CAMPBELL, *B.A.*[*]

[Abstract.]

THE circuit in which the power is to be measured is connected across the supply circuit in series with a small non-inductive resistance. By means of a transformer the small voltage on this resistance may be transformed into one whose power phase is π behind the voltage on the resistance. This is added to the voltage on the circuit to be measured, and then reversed and added again. The difference of the squares of these effective resultants is shown to be equal to a constant into the power to be measured. If there is any direct current it must be measured separately by a Weston voltmeter or other suitable instrument.

XL. *Note on obtaining Alternating Currents and Voltages in the same Phase for Fictitious Loads.* *By* ALBERT CAMPBELL, *B.A.*[*]

[Abstract.]

WHEN testing instruments for the measurement of large amounts of electrical power or energy, it is usually desirable to do so by means of fictitious loads, *i. e.*, by applying to the instrument under test current and potential-difference representing the required load. In order to obtain a fictitious non-inductive load with alternating currents, the potential difference and currents should be in the same phase. The current for the instrument under test is got by means of a transformer worked on a 100-volt circuit. The potential-difference in the same phase is got by allowing the current to flow through a non-inductive resistance, and increasing the voltage at the ends of the resistance to the required amount by means of another transformer.

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[*] Read November 9, 1900.

XLI. *On the Magnetic Field produced by Electric Tramways.*

By Prof. A. W. RÜCKER, *Sec.R.S.*[*]

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THE following calculations were made during the inquiry which has recently taken place on the Magnetic Field produced by Electric Tramways. In the course of the discussion it became evident that the gentlemen who represented the Tramway Companies had arrived at similar results; and Mr. Parry has published in the 'Electrician' for Aug. 10, 1900, a full account of this part of the theory. I had worked out both the "source and sink" and the "Fourier-Bar" theories, given below, before I was aware of the fact. The former is perhaps as accurate as the assumption that the earth is homogeneous will allow; and it was *a priori* improbable that the Fourier-Bar theory would represent the facts near the terminals of the line. The following results confirm this view; but this part of the subject was developed in consequence of a statement by the Engineers that the "Fourier-Bar" theory agreed with the results of experiments conducted by themselves, and which are not further referred to in this paper.

There is no difficulty in the calculations; and my only object in publishing some account of them is to draw attention to the fact, which is not, I think, generally recognized, that the leakage currents on a homogeneous earth affect directly only the horizontal force, while the vertical disturbing force is due only to the difference of the effects of the currents in the trolley-wires and rails or other horizontal conductors by which the current is conveyed to and from the cars. If the return conductors are insulated and parallel to the trolley-wires, the outgoing and returning horizontal currents are equal (since there is no leak), and the effects are zero at any point in the same horizontal plane as the rails, the distance of which from the line is considerable with respect to the height of the trolley-wires above the ground.

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[*] Read December 14, 1900.

The proof of these statements may be deduced directly from first principles.

If an electrical current flows from a source placed in the surface of an infinite uniform conductor bounded by a plane, the resulting magnetic field will have no component perpendicular to the surface. For if a plane be drawn through the source perpendicular to the surface it is evident, from the symmetry of the system, that the components parallel to this plane of the magnetic fields, produced by the currents on opposite sides of the plane, will be equal and opposite.

Again, let the circuit be completed by an infinite linear conductor passing through the source and perpendicular to the surface, and let the total current flowing through this conductor and diverging from the point where it meets the surface be I. The force due to the whole system at a point in the surface at a distance r from the foot of the perpendicular is $2\mathrm{I}/r$, and since half of this is due to the current in the linear conductor, the other half is due to the currents diverging from its extremity.

If we now place in the surface a sink equal to the source, the same statements hold good with regard to it; and we thus arrive at the conclusion that the current system flowing from the source to the sink has no component perpendicular to the surface, and that the component parallel to the surface is the resultant of two forces I/r and $-\mathrm{I}/r'$, where r and r' are the distances from the source and sink.

If we now regard the source and sink as the points at which the current passing through an electric motor enters the earth and returns to the generating station, it is evident that for points at some distance from the railway or tramway the trolley-wire may be represented by an insulated linear conductor joining the source and sink. The magnetic field produced by this conductor will be everywhere perpendicular to the plane surface which represents the earth, and of course can be easily calculated.

So far no attention has been paid to the rails. In reality the current flows into the soil from the rails or *vice versâ*, but however complicated the system may be it can be broken up into pairs of sources and sinks. Hence the statement is always true, that if the earth may be regarded as a homogeneous conductor, the vertical magnetic field produced by an electric railway or tramway is due solely to the differential effect of horizontal currents in the trolley-wire or other feeder and in the rails, while the horizontal magnetic field is produced solely by the stray earth-currents.

This conclusion, though almost obvious, is important. Experiment shows that the vertical-force instruments are generally those which are most seriously affected by the establishment of an electric tramway in the neighbourhood of an observatory. The question has been raised whether the observatory might be protected by a river; but the above discussion shows that the direct effect of the current in the trolley-wire could not be altered by any such natural feature of the district. All that can be said is that a want of symmetry in the earth-currents might introduce a vertical component opposed to that due to the current in the trolley-wire.

The simplest method of dealing with the rails is to regard them as an insulated conductor by which a fraction of the whole current returns to the generator. At a distance from the line considerable with respect to the height of the trolley above the road, the vertical force is practically produced by the difference between the total current I and the hypothetical uniform rail-current, the effect of which at the point considered is equivalent to the actual rail-current, the strength of which varies from point to point.

The approximate theory based on these assumptions is thus reduced to the determination of the vertical effects of a horizontal current $I(1-L)$ where L is < 1, and to the horizontal disturbances produced by a source and sink of strength LI placed in the positions of the generator and car respectively.

The effects of several cars can be obtained either by dealing with each separately or by averaging.

The calculations are quite simple and it is hardly necessary to set them forth at length.

Other things being equal, and the tramway being assumed to be straight, the vertical force disturbance increases with the length of the tramway, and for a tramway of given length the disturbance is a maximum at points on a line perpendicular to and bisecting it.

Under similar circumstances the horizontal force disturbance when the car is very distant is due only to the inflow of the earth-currents to the generating station. As the car approaches and passes the observatory the disturbance may increase and then diminish or *vice versâ*, but the total range of the magnitude of the horizontal disturbing couple (supposed to be small) depends only on the current LI and the distance of the observatory from the line (y). It is equal to LI/y.

In the case of a line of finite length the car may not reach one or both of the points at which the disturbance is a maximum or a minimum, and the range of the disturbance may therefore be reduced.

If, now, a be the length of the line (taken as straight and as the axis of x), if y be the length of the perpendicular from the observatory on the line, b and $b+a$ the distances of the ends of the line from the foot of the perpendicular from the observatory on the line, and I the total current, the disturbing forces parallel to x, y, and z (vertical) are

$$\mathrm{F}_x = \mathrm{LI}y\left\{\frac{1}{b^2+y^2}-\frac{1}{(b+a)^2+y^2}\right\}$$

$$\mathrm{F}_y = \mathrm{LI}\left\{\frac{b}{b^2+y^2}-\frac{b+a}{(b+a)^2+y^2}\right\}$$

$$\mathrm{F}_z = \frac{\mathrm{LI}}{y}\left\{\frac{b}{\sqrt{b^2+y^2}}-\frac{b+a}{\sqrt{(b+a)^2+y^2}}\right\}.$$

Experiments were made at Stockton by placing self-registering instruments at a distance of 0·4 mile from a tramway 2 miles in length, when a current of about 150 amperes was flowing along the trolley-wire over the whole length of the line.

The Vertical-force instrument showed a disturbance of 7γ ($\gamma = 10^{-5}$ C.G.S. units of magnetic force). The calculated disturbance due to the trolley-wire was 43γ.

Hence $L = 7/43 = 16{\cdot}3$ p. cent.

The Horizontal-force instrument gave

$$L = 3{\cdot}5/22 = 15{\cdot}9 \text{ p. cent.}$$

These results were in satisfactory accord, and showed that the effects produced were the same as if about 84 p. cent. of the current returned through the rails as a uniform current, and 16 p. cent. entered and left the earth at the ends of the line.

The current thus determined is such that if a uniform current of this magnitude (·84 I) flowed in the rails the disturbance produced would be equal to that actually caused by the real current in the rails which, owing to leakage, varies from point to point. It may be called the *equivalent uniform current*, and must be distinguished from the *mean current* in the rails.

The latter may be determined in two ways:

First, if $\bar{i}$ is the mean current in the rails,

$$R\bar{i} = V,$$

where R is the rail-resistance, and V the difference of potential between their extremities.

The measurements of these quantities at Stockton were undertaken rather with the view of testing whether the Board of Trade regulations were fulfilled, than for determining the mean current. The variations of the current and P.D. were too rapid, and the values of $\bar{i}$ deduced from them are not sufficiently in accord to command confidence.

The mean of 9 observations gave $\bar{i}/I = 23$ p. cent., but this value is not only deduced from discordant numbers but leads to too high a value of the disturbance at the observatory.

In the second method of calculating the mean* we may assume that the leakage at each point is proportional to the difference of potential (v) between that point and the earth. Thus if h and k be external and internal conductivities, and i_x be the current at the point x,

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* See 'Electrician,' August 10, 1900, p. 595.

$$-i_x = k\frac{dv}{dx} \qquad \text{and} \qquad -\frac{di_x}{dx} = hv,$$

whence if $\mu^2 = h/k$,

$$\frac{d^2 i_x}{dx^2} - \mu^2 i_x = 0,$$

of which the solution is

$$i_x = A\epsilon^{\mu x} + B\epsilon^{-\mu x}.$$

That is, as is shown, the problem is formally the same as that of the Fourier-Bar.

If the ends of the rails are at the points $x=0$ and $x=a$, and if the whole current (I) passes through the rails at these points

$$i_x = \mathrm{I}\frac{\epsilon^{\mu x} + \epsilon^{\mu(a-x)}}{\epsilon^{\mu a} + 1}.$$

Let now the point for which $x=0$ be at a distance b from the foot of the perpendicular drawn from the observatory to a straight line, let y be the length of the perpendicular and a the length of the line, then the vertical-force disturbance produced at the observatory by the opposing currents in the trolley-wire and rails respectively is

$$\int_0^a \frac{(\mathrm{I} - i_x)y}{\{(b+x)^2 + y^2\}^{\frac{3}{2}}} dx$$

$$= \frac{\mathrm{I}}{y}\left\{\frac{b+a}{\sqrt{(b+a)^2+y^2}} - \frac{b}{\sqrt{b^2+y^2}}\right\}$$

$$- \frac{\mathrm{I}y}{1+\epsilon^{\mu a}}\int_0^a \frac{\epsilon^{\mu x} + \epsilon^{\mu(a-x)}}{\{(b+x)^2+y^2\}^{\frac{3}{2}}} dx.$$

At Stockton the point of observation was opposite to the middle of the line so that $b = -a/2$.

Therefore the disturbing force

$$= \frac{\mathrm{I}}{y}\frac{2a}{\sqrt{a^2+4y^2}} - \frac{\mathrm{I}y}{\epsilon^{\mu a/2} + \epsilon^{-\mu a/2}}\int_0^a \frac{\epsilon^{\mu(x-a/2)} + \epsilon^{-\mu(x-a/2)}}{\{(x-a/2)^2+y^2\}^{\frac{3}{2}}} dx.$$

If now we write $x=(\lambda+1)a/2$ and $y=ua/2$ this becomes

$$\frac{4I}{au\sqrt{1+u^2}}-\frac{2Iu}{a(\epsilon^{\mu a/2}+\epsilon^{-\mu a/2})}\int_{-1}^{1}\frac{\epsilon^{\mu a\lambda/2}+\epsilon^{-\mu a\lambda/2}}{(\lambda^2+u^2)^{\frac{3}{2}}}\,d\lambda.$$

The first term in this expression is the disturbance due to the trolley-wire, which at Stockton was 43 γ. The whole expression is the actual disturbance, viz., 7 γ: hence, neglecting signs and expanding the integral in terms of $\mu a/2$, we get

$$\frac{4Iu}{a(\epsilon^{\mu a/2}+\epsilon^{-\mu a/2})}\left\{\frac{2}{u^2\sqrt{1+u^2}}+\frac{1}{2}\left(\log_e\frac{\sqrt{1+u^2}+1}{\sqrt{1+u^2}-1}-\frac{2}{\sqrt{1+u^2}}\right)\left(\frac{\mu a}{2}\right)^2\right\}.$$

It is easy to show that terms in higher powers of μ are negligible, and that the expression thus obtained is more accurate than if the denominator were also expanded.

Now at Stockton $a=2$ miles$=3{\cdot}2\times10^5$ cm., $y=0{\cdot}4$ mile, and therefore $u=0{\cdot}4$.

Substituting these values we get

$$\frac{I}{2(\epsilon^{\mu a/2}+\epsilon^{-\mu a/2})}\{11{\cdot}6+0{\cdot}715(\mu a/2)^2\}=36.$$

Neglecting the second term this gives $\mu a/2=0{\cdot}636$, and substituting this value in the second term we get $\mu a/2=0{\cdot}678$.

If we adopt the rather less accurate but more convenient plan adopted by Mr. Glazebrook, and expand throughout in terms of $\mu a/2$, the whole disturbance due both to trolley-wires and rails reduces to the form

$$\frac{Iu}{a}\left\{\log_e\frac{\sqrt{1+u^2}+1}{\sqrt{1+u^2}-1}-\frac{2\sqrt{1+u^2}}{u^2}\right\}\left(\frac{\mu a}{2}\right)^2,$$

and when $I=15$(C.G.S.), $u=0{\cdot}4$ and $a=3{\cdot}2\times10^5$ cm., as at Stockton, this was equal to 7×10^{-5}, whence

$$(\mu a/2)=0{\cdot}61.$$

If the calculations are confined to this approximation it is best to use this value of $\mu a/2$, though it is probably too small.

Having thus shown how to find $\mu a/2$ from the vertical-force disturbance, we may next use it to calculate the average current in the rails and the total leakage.

The average current between 0 and a is

$$\bar{i} = \int_0^a \frac{i_x dx}{a} = \frac{2\mathrm{I}}{a\mu}\frac{\epsilon^{\mu a}-1}{\epsilon^{\mu a}+1} = \frac{2\mathrm{I}}{a\mu}\tanh.(\mu a/2)$$

$$= \mathrm{I}\left\{1 - \frac{1}{3}\left(\frac{\mu a}{2}\right)^2\right\} \text{ approximately.}$$

The total leakage is the difference between the total current I and the minimum current at the central point (i_m).

Putting $x=a/2$ in the expression for i_u we get

$$\frac{i_m}{\mathrm{I}} = \frac{2\epsilon^{a\mu/2}}{\epsilon^{\mu a}+1} = \operatorname{sech}(\mu a/2) = 1 - \frac{1}{2}\left(\frac{\mu a}{2}\right)^2 \text{ approximately.}$$

Using the more accurate (0·678) and the approximate (0·61) values of $\mu a/2$ with the accurate and approximate formulæ respectively, we get the following results :—

		$\mu a/2 = 0·678$.	$\mu a/2 = 0·61$.
Equivalent current ...	83·9 p. cent.		
Mean current	......	86·7 p. cent.	87·4 p. cent.
Minimum current ...	......	80·6 „	81·4 „

The leakages as deduced from the equivalent and minimum currents are

16·1 p. cent., 19·4 p. cent., and 18·6 p. cent. respectively.

The general result of this discussion is that if accurate values of $\mu a/2$ are required the approximation must be carried to the second term in the integral, the other terms having their true values; but that an approximation neglecting all terms containing powers of $\mu a/2$ above the second, will give accurate values of the mean and minimum currents if the value of $\mu a/2$ used is determined to the same degree of approximation.

The evaluation of the expression

$$\frac{\mathrm{I}y}{\epsilon^{\mu a}+1}\int_0^a \frac{\epsilon^{\mu u}+\epsilon^{\mu(a-x)}}{\{(x+b)^2+y^2\}^{\frac{3}{2}}}dx,$$

may be proceeded with as follows :—

Writing
$$y=ua/2,\quad x-a/2=\lambda a/2,$$
$$b+a/2=\beta a/2,$$

the expression may be put in the form

$$\frac{2\mathrm{I}u}{a\{\epsilon^{\mu a/2}+\epsilon^{-\mu a/2}\}}\int_{-1}^{1}\frac{\epsilon^{\mu a\lambda/2}+\epsilon^{-\mu a\lambda/2}}{\{(\lambda+\beta)^2+u^2\}^{\frac{3}{2}}}\,d\lambda.$$

If we expand the integral in powers of $\mu a/2$ the general term is

$$\frac{2}{n\,!}\left(\frac{\mu a}{2}\right)^{2n}\int_{-1}^{1}\frac{\lambda^{2n}d\lambda}{\{(\lambda+\beta)^2+u^2\}^{\frac{3}{2}}}\,d\lambda=\frac{2}{n\,!}\left(\frac{\mu a}{2}\right)^{2n}\mathrm{F}_{2n}\text{ say.}$$

Then

$$\mathrm{F}_{2n}=\frac{\lambda^{2n}(\lambda+\beta)}{u^2\{(\lambda+\beta)^2+u^2\}^{\frac{1}{2}}}-\frac{2n}{u^2}\int\frac{\lambda^{2n-1}(\lambda+\beta)d\lambda}{\lambda\{(\lambda+\beta)^2+u^2\}^{\frac{1}{2}}}.$$

Multiplying and dividing the quantity under the sign of integration by $(\lambda+\beta)^2+u^2$, and writing A_{2n} for the first term, we get

$$\mathrm{F}_{2n}=\mathrm{A}_{2n}-\frac{2n}{u^2}\Big\{\mathrm{F}_{2n+2}+3\beta\mathrm{F}_{2n+1}+(3\beta^2+u^2)\mathrm{F}_{2n}$$
$$+\beta(\beta^2+u^2)\mathrm{F}_{2n-1}\Big\},$$

$$\text{or }\mathrm{F}_{2n+2}=\frac{u^2\mathrm{A}_{2n}}{2n}-3\beta\mathrm{F}_{2n+1}-\left\{3\beta^2+u^2\left(1+\frac{1}{2n}\right)\right\}\mathrm{F}_{2n}$$
$$-\beta(\beta^2+u^2)\mathrm{F}_{2n-1},$$

and when the limits are inserted

$$\frac{u^2}{2n}\mathrm{A}_{2n}=\frac{1}{2n}\left\{\frac{1+\beta}{\{(1+\beta)^2+u^2\}^{\frac{1}{2}}}+\frac{1-\beta}{\{(1-\beta)^2+u^2\}^{\frac{1}{2}}}\right\}.$$

In the particular case under consideration,

$b=a/2$, so that $\beta=0$, and we get

$$\mathrm{F}_{2n+2}=\frac{1}{n}\times\frac{1}{\sqrt{1+u^2}}-u^2\frac{2n+1}{2n}\mathrm{F}_{2n}.$$

Also

$$\mathrm{F}_0=\int_{-1}^{1}\frac{d\lambda}{(\lambda^2+u^2)^{\frac{3}{2}}}=\frac{2}{u^2}\,\frac{1}{\sqrt{1+u^2}},$$

$$F_2=\int_{-1}^{1}\frac{\lambda^2 d\lambda}{(\lambda^2+u^2)^{\frac{3}{2}}}=\log\{\lambda+\sqrt{\lambda^2+u^2}\}-\lambda(\lambda^2+u^2)^{-\frac{1}{2}}$$

$$=\log_e\frac{\sqrt{1+u^2}+1}{\sqrt{1+u^2}-1}-\frac{2}{\sqrt{1+u^2}},$$

$$F_4=\frac{1}{\sqrt{1+u^2}}-\frac{3}{2}u^2F_2,$$

$$F_6=\frac{1}{2}\frac{1}{\sqrt{1+u^2}}-\frac{5}{4}u^2F_4,\ \&c.$$

Hence approximating to the integral we get when $u=0{\cdot}4$

$$\frac{4Iu}{a(\epsilon^{\mu a/2}+\epsilon^{-\mu a/2})}\left\{11{\cdot}6+\frac{0{\cdot}715}{2\,!}\left(\frac{\mu a}{2}\right)^2+\frac{0{\cdot}758}{4\,!}\left(\frac{\mu a}{2}\right)^4+\ \&c.\right\},$$

Or, if $I=150$ amp., $u=0{\cdot}4$, $a=2$ miles $=3{\cdot}2\times10^5$ cm.,

$$=\frac{15\times11{\cdot}6}{2(\epsilon^{\mu a/2}+\epsilon^{-\mu a/2})}\left\{1+\frac{0{\cdot}0616}{2\,!}\left(\frac{\mu a}{2}\right)^2+\frac{0{\cdot}0653}{4\,!}\left(\frac{\mu a}{2}\right)^4\right.$$
$$\left.+\frac{0{\cdot}0269}{6\,!}\left(\frac{\mu a}{2}\right)^6+\ \&c.\right\}.$$

Now the coefficients of this series are much smaller and converge more rapidly than those in the expansion of

$$\frac{1}{\epsilon^{\mu a/2}+\epsilon^{-\mu a/2}}=\frac{1}{2}\left\{1-\frac{1}{2\,!}\left(\frac{\mu a}{2}\right)^2+\frac{5}{4\,!}\left(\frac{\mu a}{2}\right)^4-\frac{61}{6\,!}\left(\frac{\mu a}{2}\right)^6+\&c.\right\}$$

Hence for a given value of $\mu a/2$ a nearer approach to the true value of the expression is obtained if we take the accurate value of the exponential term and evaluate the integral to a given power of $\mu a/2$, than if we expand both expressions to that power of $\mu a/2$.

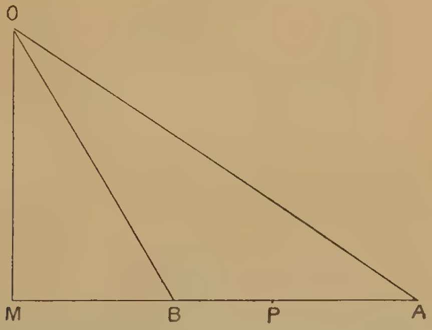
XLII. *Notes on the Practical Application of the Theory of Magnetic Disturbance by Earth-Currents.* *By* R. T. GLAZEBROOK, *D.Sc., F.R.S.*[*]

THE following notes contain some applications of Professor Rücker's theory.

In fig. 1 let MBA be the line, O the observatory, B the power-house, P the tram, and OM perpendicular on the line from O.

Then OM$=y$, MB$=b$, BP$=x$, BA$=a$. Let OB$=r_1$, OA$=r_2$.

Fig. 1.



Prof. Rücker's expression for the vertical force at O due to an element dx is

$$\mathrm{I}y\int_0^a\left\{1-\frac{\epsilon^{\mu x}+\epsilon^{\mu(a-x)}}{1+\epsilon^{\mu a}}\right\}\frac{dx}{\{(b+x)^2+y^2\}^{\frac{3}{2}}},$$

$\mu^2=h/k=$exterior conductivity/interior conductivity.

Now it will be shown that for many cases as a first approximation $\mu^2a^2/4$ may be neglected compared with unity.

On expanding in powers of μ and neglecting $\mu^2a^2/4$ in small terms, we find

$$\frac{\mathrm{F}_v}{\mathrm{I}y}=\frac{\mu^2}{2}\int_0^a\frac{x(a-x)}{\{(b+x)^2+y^2\}^{\frac{3}{2}}}dx;$$

and this evaluates to

$$\frac{\mu^2}{2}\left[\frac{1}{y^2}\{(a+b)(b^2+y^2)^{\frac{1}{2}}-b(\overline{a+b}^2+y^2)^{\frac{1}{2}}\}-\log\frac{a+b+\sqrt{(\overline{a+b}^2+y^2)}}{b+\sqrt{b^2+y^2}}\right],$$

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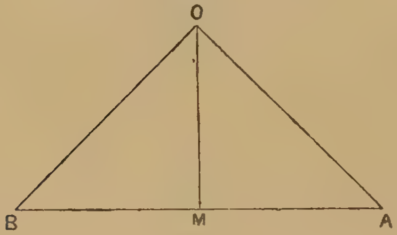
[*] Read December 14, 1900.

or
$$\frac{\mu^2}{2}\left[\frac{(a+b)r_1-br_2}{y^2}-\log\frac{a+b+r_2}{b+r_1}\right].$$

If we take the case in which $b=-\frac{a}{2}$, $r_1=r_2=r$, so that the arrangement (fig. 2) is as at Stockton,

$$F_v=\frac{\mu^2}{2}I\left[\frac{ar}{y}-y\log\left(\frac{r+\frac{a}{2}}{r-\frac{a}{2}}\right)\right]. \quad . \quad . \quad \text{(I.)}$$

Fig. 2.



From this equation the vertical force can be calculated. It is, however, somewhat complex for use. I have, therefore, examined the case in which it is supposed that the difference between flow and return current is constant along the line, the whole leak occurring at the sink. In Professor Rücker's language, I have used the equivalent uniform current.

In this case if κ be the leakage coefficient, which is the same as Prof. Rücker's $1-L$,

$$F_v=\frac{I\kappa}{y}\left\{\frac{a+b}{r_2}-\frac{b}{r_1}\right\},$$

using the same notation; or taking the above symmetrical case

$$F_v=\frac{I\kappa}{y}\frac{a}{r}.$$

In this same case

$$F_h=\frac{I\kappa a}{r^2}.$$

Now as to the value of κ.

We have from the theory developed by Mr. Parry and Prof. Rücker,

$$\kappa = \frac{\left(1-\epsilon^{-\frac{\mu a}{2}}\right)^2}{1+\epsilon^{-\mu a}};$$

and from the Stockton experiments $\mu a/2$ is about ·64 and a is 2 miles.

Hence expanding as far as $\{\mu a/2\}^4$, we find

$$\kappa = \frac{\mu^2 a^2}{8}\left(1-\frac{5}{12}\frac{\mu^2 a^2}{4}+\dots\right);$$

or neglecting $\frac{5}{48}\mu^2 a^2$ in comparison with unity,

$$\kappa = \frac{\mu^2 a^2}{8},$$

and

$$F_v = \frac{\mu^2 I}{8}\frac{a^3}{ry} = \tfrac{1}{4}\mu^2 I\frac{a^2}{y}\frac{a}{\sqrt{a^2+4y^2}}. \quad . \quad . \quad . \quad \text{(II.)}$$

It is clear that if a is 2 miles, the value of κ is about 20 per cent. too great.

To compare these two formulæ I. and II. we may, since $a/2r$ is less than unity, expand the logarithm in I.; we thus obtain

$$F_v = \frac{\mu^2 I}{8}\frac{a^3}{ry}\left\{1-\frac{1}{3}\frac{y^2}{r^2}\dots\right\}.$$

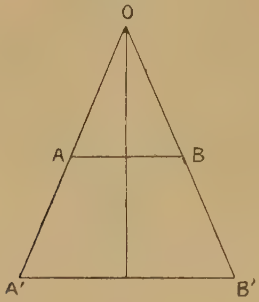
In the Stockton experiments $a=2$, $y=·4$, $r=2·04$; and the term neglected is about ·02.

A result of considerable importance may be deduced from the above formulæ.

It is clear that for similar circuits similarly placed the vertical force varies as the linear dimensions of the circuit multiplied by the current. Now if the number of cars per mile of track is to remain constant, the current must vary as the length of the track. Hence the force is proportional to the square of the linear dimensions.

Thus if we have two parallel lines AB, A′B′ (fig. 3), of which A′B′ is double the length of AB and at double the distance from the source, the effect of A′B′ is four times that of AB. This is readily seen from first principles.

Fig. 3.



For we have clearly

$$\frac{F_v}{F'_v}=\frac{\kappa I}{y}\times\frac{y'}{\kappa' I'}.$$

Also, since the number of cars per mile is constant,

$$\frac{I}{y}=\frac{I'}{y'}.$$

Moreover,

$$\frac{\kappa}{\kappa'}=\frac{y^2}{y'^2}.$$

Hence

$$\frac{F}{F'}=\frac{\kappa}{\kappa'}=\frac{y^2}{y'^2}=\frac{1}{4}.$$

Various interesting results may be obtained from the simple formula (II.), which we may write

$$F_v=\tfrac{1}{4}\mu^2a^2I\,\frac{1}{y}\frac{a}{\sqrt{(4y^2+a^2)}}.$$

Now if the number of cars per mile be constant the current varies as the length of the line. Hence

$$I=\lambda a\,;$$

and

$$F_v=\tfrac{1}{4}\lambda\mu^2a^3\,.\,\frac{1}{y}\,.\,\frac{a}{\sqrt{4y^2+a^2}}.$$

In this expression the distance y must be measured in centimetres in order to give F_v in absolute units. Hence, if we wish to measure in miles, we must introduce in the denominator a factor $1{\cdot}6 \times 10^5$, or in the numerator $\cdot 62 \times 10^{-5}$. Thus

$$F_v = \frac{\cdot 62}{4} 10^{-5} \frac{\lambda\mu^2 a^3}{y} \frac{a}{\sqrt{(4y^2+a^2)}},$$

where the lengths are now all in miles. 10^{-5} is an ordinary unit in terrestrial magnetic work denoted by γ.

With regard to the dimensions of this expression it must be remembered that $\mu^2 a^2$ is a number and λa an electric current. Thus μ^2 and λ both have dimensions in space, and in the values given for the two quantities it is assumed that each is referred to a mile run of line.

Now according to Professor Rücker's Stockton experiments the approximate value of $\mu a/2$ is $\cdot 64$, where $a=2$ miles.

Hence

$$\mu = \cdot 64, \qquad \mu^2 = \cdot 41.$$

We may compare these figures with those given by Mr. Parry in his paper in the 'Electrician' for August 10, 1900. He takes h and k to refer to the exterior and interior conductivity per unit surface and unit volume respectively, and assumes one inch as his unit of length. In his formula A is the area of the cross section of the rail, and L the area of the surface in contact with the ground per inch run of rails. Thus his quantity Lh/Ak corresponds to my h/k, with this difference, that his unit of length is the inch, mine the mile; and he finds as the value of $\{Lh/Ak\}^{\frac{1}{2}}$ the number 1/180000. Multiplying this by the number of inches in a mile, we find as the value of μ the quantity $\cdot 35$, while the leak in a line 1 mile long would be $\cdot 015$. Some other experiments give $\mu = \cdot 425$ and $\mu^2 = \cdot 18$.

The ratio of the leak to the inflowing current in a line a mile long, which is given by $\mu^2/8$, will in these two cases be $\cdot 051$ and $\cdot 0225$ respectively. By way of illustration I have made some calculations on the assumption that the leak for 1 mile is 5 per cent.; so that $\frac{1}{8}\mu^2 = \cdot 05$ and $\mu^2 = \cdot 4$, the value found at Stockton. In this case the term neglected in the original expansion is $\frac{1}{24} \times a^2$.

Let us also assume that there are 8 cars in a mile each taking rather under 20 amperes, so that

$$\lambda = 150 \text{ amperes} = 15 \text{ C.G.S. units.}$$

Hence we have

$$\lambda\mu^2 = 6.$$

Then in this case

$$\frac{\mathrm{F}_v}{\gamma} = \cdot 93 \times \frac{a^4}{y\{4y^2+a^2\}^{\frac{1}{2}}}.$$

And if we take a line a mile long at a distance of 1 mile from the observatory, we have

$$a=1, \qquad y=1, \qquad \mathrm{F}_v = \cdot 42 \times \gamma.$$

For the values at Stockton F_v is equal to $6 \cdot 2\gamma$, which is rather less than the 7γ actually found.

Instead of working with the current we may use the P.D. at the ends. Let this be V.

Then we can show that

$$\text{Leakage current} = \mu k \frac{\mathrm{V}}{2} \frac{1-\epsilon^{-\frac{\mu a}{2}}}{1+\epsilon^{\frac{\mu a}{2}}}$$

$$= \frac{ha\mathrm{V}}{8}$$

to the same approximation.

Hence

$$\mathrm{F}_v = \frac{1}{4} \frac{h\mathrm{V}}{y} \frac{a^2}{\sqrt{4y^2+a^2}}.$$

Now if the number of cars per mile is given V varies as a^2; put $\mathrm{V} = \nu a^2$, ν is the potential-difference between two points 1 mile apart.

$$\text{Hence total leak in length } a = \frac{h\nu a^3}{8}.$$

$$\text{But total} \;.\;.\;.\;.\;.\;.\;. \quad = \frac{\lambda\mu^2 a^3}{8}.$$

Therefore $h\nu = \lambda\mu^2$, an obvious result when the meaning of the quantities is considered, and

$$\mathrm{F}_v = \frac{h\nu a^4}{4y\sqrt{4y^2+a^2}} \times \cdot 62 \times 10^{-5},$$

if the quantities be all in miles.

Again we can eliminate a from these equations either by the use of the equation $\mathrm{I}=\lambda a$, or by the use of the equation $\mathrm{V}=\nu a^2$.

And we have the following four identical equations :—

$$
\begin{aligned}
\mathrm{F}_v &= \frac{\cdot 62}{4}\lambda\mu^2\frac{a^4}{y}\frac{1}{\sqrt{4y^2+a^2}}\times 10^{-5}\\
&= \frac{\cdot 62}{4}\frac{\lambda\mu^2}{y}\left(\frac{\mathrm{I}}{\lambda}\right)^4\frac{1}{\sqrt{\left(4y^2+\left(\frac{\mathrm{I}}{\lambda}\right)^2\right)}}\times 10^{-5}\\
&= \frac{\cdot 62}{4}h\nu\frac{a^4}{y}\frac{1}{\sqrt{(4y^2+a^2)}}\times 10^{-5}\\
&= \frac{\cdot 62}{4}\frac{h\nu}{y}\left(\frac{\mathrm{V}}{\nu}\right)^2\frac{1}{\sqrt{\left(4y^2+\frac{\mathrm{V}}{\nu}\right)}}\times 10^{-5}.
\end{aligned}
$$

If we wish to find the connexion between the length of the line and its distance from the observatory, so that when its effect is a maximum it may be less than a given quantity, δ say, then we must have the right-hand side of the above equations less than δ.

Now we have seen that $\lambda\mu^2/8$ is the maximum leak from 1 mile of the line. Let us call this L. Then

$$\lambda\mu^2=8\mathrm{L}\,;$$

and our equation of condition becomes

$$1{\cdot}24\times\mathrm{L}\times\frac{a^4}{y}\frac{1}{\sqrt{a^2+4y^2}}10^{-5}<\delta.$$

From this we obtain the rule :—

Calculate in absolute units the leak in a rail 1 mile long when carrying the maximum current required to drive the maximum number of cars in the mile. Let the result be L C.G.S. units of current. Then a must not exceed the value given by the equation

$$1{\cdot}24\times\mathrm{L}\times\frac{a^4}{y}\frac{1}{\sqrt{(a^2+4y^2)}}10^{-5}=\delta\,;$$

or if $\bar{\mathrm{L}}$ be the leak in amperes,

$$\bar{\mathrm{L}}=10\,\mathrm{L}.$$

Hence

$$\cdot 124\bar{L} \times \frac{a^4}{y}\,\frac{1}{\sqrt{\{a^2+4y^2\}}}\,10^{-5}=\delta.$$

If we take $\delta=\frac{1}{2}\gamma$ (a usual case in practice), this reduces to

$$\cdot 25\times\bar{L}\times\frac{a^4}{y}\,\frac{1}{\sqrt{(a^2+4y^2)}}=1.$$

With the numbers already assumed,

$$\lambda\mu^2=60 \text{ amperes},$$

and

$$L=7\cdot 5 \text{ amperes}=5 \text{ per cent. of current.}$$

If we know the resistance of a mile of the track we can calculate the potential-difference required to drive the current through, for it is clear from Mr. Parry's curves and from the theory that for a track 1 mile in length the drop required is given by the product of the current and resistance to a sufficient degree of approximation.

Now for a rail weighing 92 lbs. to the mile we may take as the resistance of a mile of continuous rail the value 0·0525 ohm. Thus, allowing for the bonds, the rails being in 36-feet lengths, about one-fortieth of the total resistance, we get as the resistance of a mile of single rail 0·0538 ohm. Hence the resistance of a double track will be 0·0135 ohm, and the potential-difference required to produce a current of 150 amperes will be about 2 volts. This, then, is the value of ν in the above formula.

We thus obtain the following table of values of a and V.

TABLE I.

y.	a.	V.
1	1·05	2·25
2	1·45	4·25
3	1·78	6·25
4	2·05	8·5
5	2·30	10·5

Or, if we take $\mu^2/8 = \cdot 0225$, so that the leak in 1 mile is $2\frac{1}{4}$ per cent., the current being 150 amperes for each mile of track, and the resistance of a mile of track 0·0135 ohm as before, we have :—

TABLE II.

y.	a.	V.
1	1·15	2·6
2	1·75	6·25
3	2·14	9·25
4	2·5	12·5

We may use the equation to find at what distance the Board-of-Trade potential-difference is innocuous, and what is the corresponding length of line. Substituting in the fourth equation $V=7, \nu=2$, and $h\nu=6$, I find

$$y=3\cdot 28 \text{ miles.}$$

And since $V=\nu a^2$, the corresponding length of line will be $\sqrt{3\cdot 5}$, or 1·87 miles. Thus in round numbers 2 miles of track carrying a current of 300 amperes with a potential-difference of 7 volts between the ends might produce a vertical magnetic force of $\cdot 5 \times 10^{-5}$ units on an observatory at a distance of 3 miles.

If we remember that λ is the current required to drive the cars in a mile of line, we can put the rule thus :—

Multiply the current in amperes required to drive the cars in a mile of line by the number $\frac{1}{10}\mu^2/8$. Let the result be J amperes. Then the maximum value of a is given by

$$2\cdot 5\,\mathrm{J}\frac{a^4}{y}\cdot\frac{1}{\sqrt{(a^2+4y^2)}}=1.$$

According to the figures assumed in Table I. above the value of $\mu^2/8$ is ·05.

Again, we have

$$h\nu=\lambda\mu^2=\frac{\lambda h}{k}.$$

Hence $$\lambda=k\nu,$$

as is obvious from the definitions.

The value of $1/k$ is, as we have seen, ·0135 ohm; and since $\mu^2 = h/k$, we have

$$\frac{1}{h} = \frac{1}{\mu^2 k} = \cdot 034 \text{ ohm approximately.}$$

Of course if a lower value be assumed for μ^2 the value of $1/h$ is proportionately raised.

Again, for rails of similar cross-section h varies as the linear dimensions of the cross-section, and k as the square of the same. Hence μ^2 varies inversely as the linear dimensions, and the leak is reduced for a given current by increasing the area of the rail.

Appendix added January 1901.

An important paper was read before the German Physical Society in Berlin in June 1899 by J. Edler (*Verhandl. des Deutschen physikal. Gesellsch.* i. Jahrg. No. 10), describing a series of experiments in which the magnetic disturbances due to a line at Spandau were measured at a number of stations at different distances from the line; and it occurred to me to apply the above theory to the results. The line is approximately straight, and is about 5 kilometres in length. The current is said to have varied between 35 and 150 amperes. I have assumed in the calculations a mean current of 100 amperes, the voltage being 500 volts. I also assumed the value of the leak-coefficient for a mile of line to be ·025, corresponding to the lesser of the two values for which tables are calculated in the paper. The value of μ^2 which corresponds to this leak is, when the distances are measured in kilometres, approximately equal to ·08, and the leak in a length of a kilometres is $\cdot 01 a^2$. The results for the vertical disturbance are given in Table III., in which the first column gives the distance of the observing-station from the line in kilometres, the second column the calculated, and the third the observed values of the force, the unit being as usual 10^{-5} Gauss.

It is clear that at the two shorter distances the formula fails to represent the facts.

In the case of the next four stations, that is for a range

TABLE III.

y.	F calculated.	F observed.
·38	12·8	23·17
·64	7·3	10·6
·79	5·8	5·6
·92	4·9	4·3
3·01	·99	·95
7·48	·21	·24
1·54	1·5	1·04

from ·79 to 7·48 kilometres, or from half a mile up to five miles, the agreement is practically exact.

In the case of the experiment recorded in the last line the river Havel, which from a small map printed with the paper is apparently nearly half a kilometre in width, and another smaller stream lie between the observing-station and the line. This may possibly account for the discrepancy between theory and experiment.

It is easy from Professor Rücker's theory to calculate the horizontal resultant disturbance. Taking, as in fig. 1, A and B to be the source and sink and O the observatory, we have to find the resultant of two forces Iκ/OB and Iκ/OA acting at right angles to OB and OA respectively, in such a way that if the one tends to increase the angle MBO the other tends to decrease the angle MAO.

This resultant is easily shown to be equal to

$$\frac{\mathrm{I} \,.\, \kappa \,.\, a}{r_1 \,.\, r_2}.$$

To apply this I have assumed the whole leak to take place at the ends of the line, which is clearly quite an extreme case, and have thus obtained the following table.

In this case the discrepancy is very marked. The observed and calculated forces are quantities of the same order; and that is all that can be said. Possibly this may be due to the very close proximity of the river which runs parallel to the

TABLE IV.

y.	H calculated.	H observed.
·38	2·25	9·5
·64	2·15	6·09
·79	2·08	4·67
·92	1·92	4·31
3·01	·83	1·33
7·48	·21	·44
1·54	1·56	1·44

line. The horizontal disturbance is due to the vertical component of the leakage-current. We may possibly look upon the river as an extended sink. Currents which start in a horizontal direction from the side of the rail opposite to the river may be diverted by it, gradually becoming vertical, and finally, after having the direction turned through 180°, passing horizontally, or nearly so, back under the rail and into the river; or it may be that the water-surface under the ground is not very far below the level of the rails—the observing-stations were in most cases only 3·5 metres above the water-level,—and that in consequence of this the lines of flow are inclined at a less angle to the vertical than they would otherwise be.

The presence of the river ought clearly to affect the horizontal disturbance more than the vertical.

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XLIII. *On Electric Inertia and the Inertia of Electric Convection.* *By* ARTHUR SCHUSTER, *F.R.S., Professor of Physics at Owens College, Manchester**.

1. OUR calculations of self-induction are based on the assumption that the currents which traverse a conductor fill it continuously, the flow being treated as that of an incompressible liquid. The assumption is generally recognized not to hold in the case of electrolytes, where electricity is conveyed by a number of irregularly distributed ions. In the immediate neighbourhood of such an ion, the magnetic field will be many times greater than that calculated on the supposition of continuous distribution, and hence the total magnetic energy is underestimated. What is universally recognized in the case of electrolytes must also be conceded when the current is conveyed by a gas, and the idea is gaining ground that even in solid conductors the current consists of moving positive and negative electrons.

It is the object of this paper, to calculate the additional terms which become necessary for the evaluation of self-induction, and to discuss the possible cases in which the corrections may affect experimental results.

2. I begin by calculating the total energy of a number of electrically charged, equidistant particles, placed in a straight row and all moving with the same speed (u). If the charge (q) of each particle is taken to be spread uniformly over a spherical surface of radius a, the magnetic energy is $q^2u^2/3a$†, so that the particle behaves as if it had a mass $2q^2/3a$. Without making any assumption, as to whether the magnetic forces are to be taken as vanishing within the electron or not, we may use the above expression, taking a to be a linear quantity, not necessarily the radius of the electron but of the same order of magnitude. If there are n particles per unit length at a distance d apart so that $nd=1$, the energy per unit length will be $q^2u^2/3a$, as far as the magnetic field established by each particle is concerned. The mutual energy of different

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* Read December 14, 1900.

† Heaviside, Phil. Mag. April 1889, p. 324.

particles has to be added in order to obtain the total magnetic energy. A pair of particles at a distance r from each other will have a mutual energy of q^2u^2/r, and each particle with its nearest neighbour on either side will therefore contribute a term $2e^2u^2/d$. Taking the remaining particles in pairs we get for the mutual energy of a central particle and p pairs on either side

$$\frac{2q^2u^2}{d}\left(1+\tfrac{1}{2}+\tfrac{1}{3}+\ldots\frac{1}{p}\right)=\frac{2q^2u^2\mathrm{S}}{d}.$$

The series S may be added up and the result expressed in the form

$$\mathrm{S}=\mathrm{B}+\log p,$$

where B is a number approximately equal to 0·577.

If p is very large, the total magnetic energy per unit length of the central portions of the row will be

$$n^2q^2u^2\left(2\mathrm{S}+\frac{1}{3an}\right)=\mathrm{C}^2\left(2\mathrm{B}+2\log p+\frac{1}{3an}\right), \quad . \quad (1)$$

where C stands for the current.

3. I now compare this expression with that calculated on the usual supposition, which is, that the electrification is not confined to electrons but fills continuously a rectangular space having a square cross-section with sides equal to d, and having a length equal to $(2p+1)\,d$, for which we write 2D. The total magnetic energy in this case will be the same as that of two linear conductors of the same length, and at a distance apart which is equal to the geometric mean of the square section r_0 where

$$r_0=\cdot 447\,d.$$

For unit current in each of the conductors, the linear elements of which are ds_1, ds_2, the magnetic energy between the conductor s_2 and the element ds_1 is

$$ds_1\int ds_2\left(\frac{1}{r}+\frac{1}{2}\,\frac{d^2r}{ds_1\,ds_2}\right).$$

The well-known ambiguity, as to the expression under the integral sign, disappears in our case, because we are only comparing the magnetic energy on two suppositions, and must therefore consistently use in both cases the same expression for the mutual energy of two current elements. As D is large, the value of $\frac{dr}{ds_1}$ for small values of s_1 will be sensibly equal to ∓ 1 according as s_2 is large on the positive or negative side, and consequently we find the above expression to be equal to

$$ds_1\left(-1+\int_0^{\mathrm{D}} \frac{2ds_2}{\sqrt{r_0^2+s_2^2}}\right)$$

or

$$2ds_1(\log(\mathrm{D}+\sqrt{r_0^2+\mathrm{D}^2})-\log r_0-\tfrac{1}{2}). \quad . \quad . \quad (2)$$

We may substitute pd for D, and the above expression then becomes, neglecting r_0 compared with D,

$$ds_1\left(2\log\frac{2pd}{r_0}-1\right).$$

The bracket being independent of s_1 we conclude that the central portions of the column have a magnetic energy which for a current C and unit length is

$$\mathrm{C}^2\left(2\log p+2\log\frac{2d}{r_0}-1\right)=\mathrm{C}^2(2\log p+1{\cdot}996).$$

The excess of (1) over this will be the required difference in the magnetic energy. Introducing the numerical value for B this difference becomes

$$\mathrm{C}^2\left(\frac{1}{3an}-{\cdot}842\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This expression being proved for any portion of the circuit which can be considered straight for a length which is large compared with the distance between the electrons, may be taken to hold for the complete circuit, as, excluding sharp angles, every circuit may be divided into portions satisfying this condition.

4. Some additional explanation is necessary for ordinary conductors whose cross-section is many times larger than the distance d between the electrons. The cross-section of such conductors may be divided into square elements, each square having sides equal to d. If we imagine the electrons to be placed at the centre of each square we may calculate the mutual energy of any two parallel columns and thus obtain

further correcting terms. It is easily seen that these terms will be positive and tend to diminish the negative term in (3). They will also be small and of the same order of magnitude as other quantities we neglect. It serves no useful purpose therefore to calculate them out in detail. If A is the area of the cross-section, the number of electrons spread over it will be An^2, so that the total correction to the magnetic energy becomes

$$An^3q^2u^2\left(\frac{1}{3a} - \frac{\cdot 842}{d}\right).$$

If d is large compared with a the second term may be neglected. In that case, writing i for the current-density n^3uq, and N for n^3 which represents the number of electrons in unit volume, we obtain for the correcting term per unit volume of the conductor

$$\tfrac{1}{2}\mu i^2,$$

where μ stands for $2/3a\mathrm{N}$.

The flow of electricity will behave, therefore, as if it had inertia, the apparent mass for unit current-density and unit volume being μ. The dimension of μ, as pointed out by Hertz, is the same as that of a surface.

We may conveniently use the expression "electric inertia" for the quantity μ; the energy due to electric inertia is the energy of the magnetic field due to the moving electrons over and above that which is calculated in the usual way.

5. The investigation has been restricted to the case of a number of electrons moving in one direction, with the same speed and keeping the same equal distances from each other, but the result holds more generally. The magnetic field established by a positive electron moving in one direction is the same as that of a negative electron moving with the same speed in the opposite direction. Superposing on our system of one kind, a second one carrying opposite electricity in the opposite direction, N being the number of electrons of each kind and Ai_1, Ai_2 the currents conveyed in the two directions, the energy per unit volume becomes

$$(i_1^2 + i_2^2)/3\mathrm{N}a$$

or

$$\mu = \frac{i_1^2 + i_2^2}{(i_1 + i_2)^2} \cdot \frac{2}{3\mathrm{N}a}.$$

The assumption that two sets of electrons move so as to keep equal relative distances is not of course satisfied. The change in the relative distance will increase the mutual energy between the electrons, but the increase will be of the order of magnitude which we have neglected, and the term we have retained is not affected by the relative distances of the electrons. For the purpose of this paper it is not therefore necessary to go beyond the above expression.

The correction to self-induction for a conductor of length l and uniform cross-section A will be $\frac{1}{2}\frac{\mu l}{A}$ or

$$l\{1+2\kappa(\kappa-1)\}/3NAa,$$

where κ is that fraction of the total current which is conveyed by the positive electricity. If both kinds of electrons take equal parts in conveying the current, the correction becomes

$$l/6NAa,$$

The correcting term increases in importance with diminishing cross-section, and might be made large, if the cross-section could be reduced so as to be comparable with molecular dimensions.

6. We must now enter into a discussion of the numerical quantities involved. In the case of metallic conductors we may, in the absence of contrary evidence, reasonably take N to be of the order of magnitude of the number of molecules per unit volume. Taking the molecular distance to be 10^{-8} this gives $N=10^{24}$.

As regards the linear quantity a, observations made on cathode rays determine it, in my opinion, and in any case fix a lower limit. The deflection of these rays by the magnet shows that the moving electron itself has inertia or is carried by a small mass. J. J. Thomson adopts the latter view, but it seems to me to be more natural to take the inertia of the cathode particle to be the magnetic inertia of the electron. If m is the mass, real or apparent, of the particle carrying the negative charge, we may determine the ratio q/m. Measurements of this quantity were first made by myself in 1889 *, and since then more accurate determinations by my

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* Bakerian Lecture, Proc. Roy. Soc. vol. xlvii. p. 526 (1890).

original method or by other and better methods have been carried out by J. J. Thomson, Kaufmann, Lenard, and Wiechert. Taking the latter's estimate as being deduced from the most direct method, I shall use $1{\cdot}3 \times 10^7$ in electromagnetic measure for the value of q/m. If q, as was assumed by me and afterwards proved by J. J. Thomson, is the same quantity as that carried by the ion in a liquid, we know that in the case of *e. g.* hydrogen $q/m' = 10^4$, if m' denote the mass of an atom of hydrogen. Now from the density ρ of the gas and the number N$'$ of hydrogen molecules per unit volume, we may calculate $2m' = \rho/\mathrm{N}'$. Taking $\rho = q \times 10^{-5}$, $\mathrm{N}' = 21 \times 10^{18}$, we find $m' = 2 \times 10^{-24}$, and hence $q = 2 \times 10^{-20}$ *.

Also

$$a = \frac{2q}{3} \cdot \frac{q}{m} = \frac{2}{3} \times 2 \times 10^{-20} \times 1{\cdot}3 \times 10^7 = 1{\cdot}8 \times 10^{-13}.$$

The linear dimension of the electron would therefore have to be about thirty-thousand times smaller than the molecular distance in solids, but I can see nothing more astonishing or improbable in this than in the alternative assumption of particles having masses thirteen-hundred times smaller than the masses of hydrogen atoms.

The electric energy per unit volume and unit current-density was found to be $1/3a\mathrm{N}$, which in the case of solid conductors would therefore become 2×10^{-12} C.G.S. units. We possess fortunately a series of experiments by Hertz in which he investigated the possibility of electric inertia, and found that if it exists it must be smaller than 18×10^{-8} for unit current-density and unit volume. The effect we have calculated is much smaller than the number given by Hertz, and as this represents the limit beyond which he could not push his experiments, we must for the present give up the hope of testing the results of our theory. There seems only one chance—and not at all an impossible one—that in some cases the effects may be considerably larger than those calculated above. Perhaps in some bad conductors like carbon, the distance between the moving electrons is greater than the distance between the molecules. If it is fifty times as great, we should get within the limits to which Hertz worked.

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* Owing to some arithmetical blunder, this quantity was put down as 3×10^{-23} in my Bakerian Lecture.

7. In the case of electrolytes the electric inertia of moving ions is small compared to their mass inertia. The latter must to some extent affect the motion of electricity in electrolytes, and it becomes a matter of interest to obtain, if possible, some experimental evidence to establish the effects of this mass inertia.

If N molecules of a dissociated salt are dissolved in unit volume of water, and if u_1, u_2 represent the velocities of the ions having masses m_1, m_2, the energy per unit volume is

$$\tfrac{1}{2}\mathrm{N}(m_1u_1^2+m_2u_2^2).$$

If the masses of the ions contained in each molecule referred to hydrogen are a_1, a_2, and α represents the ratio between the mass and charge for a hydrogen atom, which is numerically equal to $10{\cdot}4\times10^{-5}$,

$$m_1=a_1\alpha q, \quad m_2=a_2\alpha q.$$

Introducing the current-density

$$i=\mathrm{N}q(u_1+u_2),$$

and the weight p of dissociated molecules per unit volume, which is related to the other quantities used by the equation

$$p=\mathrm{N}(m_1+m_2)=\mathrm{N}\alpha q(a_1+a_2),$$

we obtain for the energy of ionic motion

$$\tfrac{1}{2}\mu i^2=\frac{1}{2}\frac{a_1+a_2}{p}\alpha^2\left[\frac{a_1u_1^2+a_2u_2^2}{(u_1+u_2)^2}\right]i^2.$$

If u_1 refers to the kation, the ratio u_2/u_1+u_2 is Hittorf's constant deduced from the migration of ions. Denoting this by n we have finally

$$\mu=\frac{a_1+a_2}{p}\alpha^2(a_1(1-n)^2+a_2n^2).$$

Taking for instance nitrate of silver, for which $n={\cdot}53$, $a_1=108$, $a_2=62$, the energy of ionic motion per unit volume and unit current becomes equal to $3{\cdot}8\times10^{-5}/p$, where p is the number of grams of nitrate of silver per c.c. of water. Hertz gives in the paper quoted for the same salt the number $7{\cdot}8\times10^{-5}$, which is nearly double the value I find. As Hertz does not indicate his method of calculation, it is not now possible to trace the discrepancy, unless there is some slip in the above reasoning.

In order to discuss the possibility of an experimental verification of the increase in self-induction due to electric inertia, we may consider two narrow tubes placed side by side. If he tubes have an internal diameter of 1 mm., their axes might be placed 2 mm. apart and the coefficient of self-induction would in that case be equal to 6·6 per cm. of the double conductor. The ionic inertia would increase the value by $7{\cdot}6\times10^{-5}/p\mathrm{A}$, which is nearly equal to 1 if $p=\cdot01$, The increase in self-induction amounts therefore to about 15 per cent., but the whole quantity is so small that it could not be measured very accurately.

When the dilution of the electrolyte becomes great, the ionic inertia may become considerable. Thus in the case of the purest water obtained by Kohlrausch, he estimates that there was ·08 mg. of dissociated hydrogen per cubic metre This gives $p=7{\cdot}2\times10^{-10}$.

In order to avoid making any assumption as to the quantity n, we may substitute that value for it which gives the smallest value to μ. This is found to be $n=a_1/(a_1+a_2)$, so that if

$$a_1=2,\quad a_2=16,\quad \alpha^2=108\times10^{-10},\quad p=7{\cdot}2\times10^{-10},$$

$$\mu=\frac{a_1a_2}{p}\cdot\alpha^2=480.$$

The energy of straight parallel currents close together as in the above example would therefore in this case be almost entirely due to the ionic motion, but it will appear in § 9 that the chances of experimental verification are not very great, as long as an increase in the value of μ is accompanied by a corresponding increase in the resistance.

8. The case of gases presents several features of special interest. The effect of inertia on the deflection of the cathode ray has already been alluded to, and the fact that in the positive portion of the discharge, the current is conveyed by a comparatively slow diffusion of molecules has been proved by me in 1885*. In the positive part of the discharge the number of ions is proportional to the current, as follows from Hittorf's experiments. To make an estimate of the inertia involved

* Bakerian Lecture, pp. 548, 550.

in the diffusion, I take as an example one of my experiments for which I have calculated approximately the ratio of the number of ions to the total number of molecules as $1{\cdot}2 \times 10^{-6}$ at a pressure of $\frac{1}{3}$ mm., at which the density of nitrogen is 5×10^{-7}. The quantity called p above is in this case 10^{-13}, and taking $a_1 = a_2 = 7$,

$$\mu = 49 \times 10^{13} a^2 = 5{\cdot}4 \times 10^6.$$

This value holds for a current-density of $1{\cdot}5 \times 10^{-4}$, and will be inversely proportional to the current-density.

The electric energy of convection in gases may therefore be very large and exceed many times the magnetic inertia calculated on the usual hypothesis. As an example, I take a circular tube of radius r bent into the form of a circle of radius R, and as a first approximation we may take the expression

$$\mathrm{L} = 4\pi \mathrm{R}\left(\log \frac{8\mathrm{R}}{r} - 1{\cdot}75\right);$$

the electric energy of convection per unit current is $\mu \mathrm{R}/r^2$, so that the total energy per unit current becomes

$$\frac{\mathrm{R}}{r^2}\left[\mu + 4\pi r^2\left(\log \frac{8\mathrm{R}}{r} - 1{\cdot}75\right)\right].$$

With $r=1, \mathrm{R}=10$ the numerical value of the second term is 34, and this term is therefore quite insignificant compared with the first. A coil might be made of a good many windings still leaving the inertia of convection great compared to the magnetic inertia. In any problem in which the self-induction of gases has to be calculated, the ordinary methods would give erroneous results.

9. The general equations of electric motion will be altered by the introduction of the inertia, whether it be the inertia of the electron or, as in the case of liquids or gases, the inertia of the ion.

If E represents the component of electric force in any one direction, and u the flow in the same direction, the ordinary equations of electric motion are

$$\rho u = \mathrm{E},$$

with two other equations giving the components in two other directions, ρ being the resistivity of the medium. If, however, the electric flow possess inertia, the electric forces will be doing work in increasing the energy of convection, the rate of doing work per unit volume being $\mu u\dot{u}$. Hence the complete equation will be

$$\rho u+\mu\dot{u}=\mathrm{E}.$$

In the case of conductors, we may put

$$\mathrm{E}_1=-\left(\frac{d\psi}{dx}+\frac{d\mathrm{F}}{dt}\right),$$

ψ being the electrostatic potential and F the X component of the vector potential, and introducing the conductivity κ for $1/\rho$, the equation becomes

$$u+\kappa\left(\frac{d\mathrm{F}}{dt}+\frac{d\psi}{dx}\right)+\kappa\mu\frac{du}{dt}=0,$$

or, as $\nabla^2\mathrm{F}=-4\pi u$,

$$4\pi\kappa\left(\frac{d\mathrm{F}}{dt}+\frac{d\psi}{dx}\right)=\nabla^2\mathrm{F}+\kappa\mu\frac{d}{dt}\nabla^2\mathrm{F},$$

with the corresponding equations for the other components of the vector potential. The electrostatic potential disappears in the usual way by introducing the components of magnetic induction (a, b, c) for those of vector potential, the typical equation in that case being

$$4\pi\kappa\frac{da}{dt}=\left(1+\kappa\mu\frac{d}{dt}\right)\nabla^2 a.$$

If the flow is periodic so that a, b, c are proportional to e^{ipt}, where i stands for $\sqrt{-1}$, we obtain by dividing out the time factor

$$\nabla^2 a=\frac{4\pi\kappa ip}{1+\kappa\mu ip}a.$$

This equation shows that the inertia will affect the magnetic induction and consequently the lines of flow only when $\kappa\mu p$ becomes an appreciable fraction. But μ itself we have found small in liquids and solids, while κ is never greater than 10^{-3}. Hence $\kappa\mu p$ cannot produce appreciable effects until p becomes of the order of magnitude which holds for luminous radiations. But that case will require separate treatment as our equations are not correct for rapid variations of the currents.

In the numerical example given in § 8, μ was found to be equal to $5{\cdot}4 \times 10^6$ for a current-density of $1{\cdot}5 \times 10^{-4}$. The product $\kappa\mu$ in the case considered will be independent of the density. The fall of potential in the experiment was 5 volts per cm., so that the conductance was $\cdot 3 \times 10^{-12}$, and the cross-section being 2 the product $\kappa\mu$ becomes $\cdot 8 \times 10^{-6}$. This product would be considerably larger at lower pressures, and when the frequency is of the order of magnitude of leyden-jar discharges it is very likely that the term depending on the inertia of convection is very appreciable. Some of the facts brought to light in J. J. Thomson's work on luminous discharges produced by induction in tubes without electrodes seem to point in that direction. When $\kappa\mu p$ becomes large compared to unity, the equation reduces to

$$\nabla^2 a = \frac{4\pi a}{\mu},$$

so that, for instance,

$$a = e^{-\sqrt{\frac{4\pi}{\mu}}x} \cos pt$$

would represent a possible disturbance.

10. The effects of inertia may become very appreciable in the case of luminous vibrations, to which our equations do not apply, as the term depending on the specific inductive capacity has been left out of account. In forming the more complete equations a difficulty presents itself which is due to the fact that the displacement currents may also to some extent have inertia or what is equivalent to inertia. The apparent masses will not be in general the same as those involved in the conduction currents, though in the case of displacements of electrons in the molecules, the order of magnitude may be the same.

If $\frac{1}{2}\mu' i^2$ represent the energy per unit volume due to electric inertia where i is the displacement current, the complete equations for the magnetic induction become, for a medium of specific inductive capacity K and conductivity κ,

$$\left(1 + \mu\kappa \frac{d}{dt} + \frac{\mu' \mathrm{K}}{4\pi} \frac{d^2}{dt^2}\right) \nabla^2 a = \mathrm{K} \frac{d^2 a}{dt^2} + 4\pi\kappa \frac{da}{dt}$$

with the two corresponding equations for b and c.

If a varies proportionally to e^{-ipt} this reduces to

$$\left(1 - i\mu p\kappa - \frac{\mu' \mathrm{K} p^2}{4\pi}\right)\nabla^2 a = -(\mathrm{K}p^2 + 4\pi\kappa i)a.$$

In non-conductors the terms involving κ disappear, and $a = e^{iqx}$ is a solution provided that

$$q^2\left(1 - \frac{\mu' \mathrm{K} p^2}{4\pi}\right) = \mathrm{K}p^2,$$

which gives for the velocity of propagation p/q the equation

$$\frac{p^2}{q^2} = \frac{1}{\mathrm{K}} - \frac{\mu'}{4\pi}p^2;$$

dividing by V^2, where V is the velocity of light in vacuo, we obtain for the refractive index of the medium (n)

$$\frac{1}{n^2} = \frac{1}{\mathrm{K}\mathrm{V}^2} - \frac{\mu'\pi}{\lambda^2}.$$

If the second term is small we find to the first approximation, writing n_0 for $\mathrm{V}\sqrt{\mathrm{K}}$,

$$n = n_0 + \frac{\mu' \pi n_0^3}{\lambda^2} + \dots.$$

J. Willard Gibbs * nearly twenty years ago deduced from the mere assumption that the medium possesses a fine-grained structure an equation for the relation between velocity of wave-propagation and wave-length which is identical with the above, and it was pointed out by him that his equations include the case in which the medium is endowed with electric inertia.

It seems of interest to determine the order of magnitude of the quantity μ'. The coefficient of $1/\lambda^2$ may be calculated from the optical dispersion and for ordinary flint-glass is found to be about 10^{-10}, the corresponding value of n_0 being about 1·6. Hence $\mu' = 10^{-11}$ approx. This value does not differ very materially from 2×10^{-12}, which is the estimate of μ which has been made for solid conductors in § 6. As the latter estimate depends on the cube of molecular distance which was assumed to be 10^{-24}, the difference between the two numbers falls within the possible errors of estimation.

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* American Journal of Science, vol. xxiii. p. 262 (1882).

I do not, however, attach much importance to the apparent equality of the numbers and mention it only as a remarkable coincidence, which probably is accidental. As the quantity called μ diminishes with increasing distance between the molecules, and for gases at atmospheric pressure would be 50,000 times smaller than for liquids, there would be a very wide discrepancy between μ and μ' in the case of gases. Should the coincidence between μ and μ' in solids prove to be more than accidental, it would prove that the greater part of the kinetic energy in a luminous vibration traversing a transparent solid is accounted for by the kinetic energy of the electrons attached to the molecules and set in motion by the vibration. This proposition is obviously not true in the case of gases, but may hold for solids.

It would be of some interest to discuss the effects of metallic reflexion in connexion with the equations which are given at the beginning of this paragraph. H. A. Lorentz * has already introduced a term depending on inertia in the equations of motion of light, and pointed out that without such inertia the electromagnetic theory of light could not explain the known experimental facts. But even the inertia term introduced by Lorentz, was not sufficient to account for all the discrepancies between theory and experiment. My equations differ from those of Lorentz by the introduction of two constants μ and μ' which need not be identical, for there is no *a priori* reason why the inertia of the conduction current should be the same as that of the displacement current. The numerical results of Lorentz's investigation are not easily interpreted, as he used the Helmholtz form of the equations, which involves a large and unknown coefficient.

Attention may be drawn in conclusion to several papers by P. Drude † "On the Electron-theory of Metals."

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* *Zeitschrift für Math. u. Physik*, vol. xxiii. p. 197 (1878).

† *Annalen der Physik*, vol. i. p. 566, vol. iii. p. 369, and *Physik. Zeitschrift*, vol. i. p. 161.

XLIV. *On Magnetic Precession.* *By* ARTHUR SCHUSTER, *F.R.S., Professor of Physics at the Owens College, Manchester* *.

1. IN a previous paper † I discussed the possible effects of electric inertia, confining myself to the case of conductors at rest. But Hertz, in his interesting experiments on the subject, showed that the most delicate method of investigating the influence of inertia is based on the apparent electromotive forces which are introduced by the motion of conductors. If electricity possesses inertia, the rotation of a body through which currents pass, affects the flow of these currents in the same manner as the earth's rotation affects the direction of currents of air on its surface.

Hertz obtained only negative results, but could fix an upper limit to the possible inertia of electric currents. It occurred to me that this inertia, even if below the limits given by Hertz, might show accumulated effects, when the currents last for a sufficient time. If the earth's magnetism be due to electric currents, general considerations suggested to me that the effects of inertia might explain the secular variation. The following investigation shows that indeed inertia would cause a "magnetic precession" precisely of the character of the secular variation, but that this precession would be very much slower than the variations which are actually observed.

2. If m is the *mass* of positive electricity in unit volume, and u the velocity, the energy of an electric current, so far as it depends on this mass, would be mu^2 per unit volume, assuming for the sake of simplicity that positive and negative electricity move with the same velocity. If i is the current-density, we may substitute $\frac{1}{2}\mu i^2$ for this energy, where μ has the same meaning as in my previous paper. If q is the quantity of positive electricity in unit volume the current-

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* Read December 14, 1900.

† *Ante*, p. 629.

density is $2qu$, so that

$$4q^2u^2 = i^2,$$

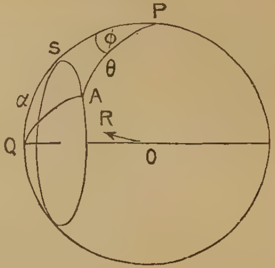
$$\therefore \quad 2q^2\mu = m.$$

The momentum of positive electricity will be mu or $q\mu i$.

If a mass moves relatively to a body which is rotating, we may treat the effect of the rotation as being the same as that due to certain fictitious forces. These fictitious forces are of two kinds. The first, depending on the square of the angular velocity and commonly called centrifugal force, will act equally on positive and negative electricity, and cannot therefore produce any effect on the distribution of electric currents. The second force depends on the relative velocity, it will therefore have opposite effects on positive and negative electricity, in other words it will be equivalent to an electromotive force. Its direction is at right angles both to the direction of relative velocity and to the axis of rotation, and its intensity per unit mass is equal to $2\omega v_r \sin\chi$, where ω is the angular velocity, v_r the vector representing the relative velocity, and χ the angle between v_r and the axis of rotation. The direction of the force is such that the displacement of the body through a right angle in the direction of rotation would bring the direction of the force into the plane containing the axis of rotation and the direction of relative velocity.

If electric currents are confined to the surface of a sphere rotating with an angular velocity ω, we may calculate the components of electromotive force produced by the rotation of the sphere, but it is only the tangential components which will produce any effect. For any point on the earth which has a colatitude θ, the horizontal components will be the same, as if the angular velocity were $\omega\cos\theta$ about the vertical. If the flow is from north to south, the force will be to the west in the northern hemisphere, and its intensity per unit volume will be $2m\omega\cos\theta\, u_S$, u_S denoting the velocity to the south. For flow u_E from west to east the force will be $2m\omega\cos\theta\, u_E$ and act from north to south in the northern hemisphere. Hence, if we take the directions to south and to east as the positive directions the two forces will be $-2m\omega\cos\theta\, u_S$ and $+2m\omega\cos\theta\, u_E$. These are the forces per unit volume; to obtain the forces per unit quantity of electricity we divide by q, and replacing the velocities of flow by the current-densities we have for the two components $-2\mu\omega i_S \cos\theta$ and $2\mu\omega i_E \cos\theta$. These forces are of the nature of electric forces, and their effects may be calculated if the components of i are known.

Fig. 1.



3. In the simplest and most important case, the currents are such as to produce a magnetic field identical on the outside with that of a uniformly magnetized sphere, the axis of magnetization passing through the equator. Let O Q (fig. 1) be the axis of magnetization. The currents will all lie in planes at right angles to that axis. If A S is a portion of such a current and we write :

α, for the arc QS or Q A ;
ϕ, for the angle S P A ;
θ, for the colatitude P A ;
a, for the radius of the sphere ;

the current function will be

$$a\mathrm{I}\cos\alpha = \mathrm{I}a\cos\phi\sin\theta.$$

Hence the component currents are :

Easterly component

$$= -\frac{d}{d\theta}\mathrm{I}\cos\phi\sin\theta = -\mathrm{I}\cos\phi\cos\theta \;.\;\;.\;\;. \quad (1)$$

Southerly component

$$= \frac{d}{\sin\theta\, d\phi} - \mathrm{I}\cos\phi\sin\theta = -\mathrm{I}\sin\phi. \;\;.\;\;. \quad (2)$$

These are components of currents per unit length of linear cross-section at any point ; to obtain current-densities we must divide by t, the thickness of the shell through which we imagine the currents to flow. If we write Ψ_S and Ψ_E for the electric forces acting towards the south and east respectively, we have therefore

$$\Psi_S = -2\mu\omega\mathrm{I}\,.\cos^2\theta\cos\phi/t,$$
$$\Psi_E = \quad 2\mu\omega\mathrm{I}\cos\theta\sin\phi/t.$$

Now

$$2\cos^2\theta\cos\phi = \cos\phi(1+\cos 2\theta) = \cos\phi + \frac{d}{d\theta}\left(\tfrac{1}{2}\cos\phi\sin 2\theta\right)$$

and

$$2\cos\theta\sin\phi = \cos\theta\sin\phi - \frac{d}{\sin\theta\, d\phi}\left(\tfrac{1}{2}\cos\phi\sin 2\theta\right).$$

Hence we may divide the electric forces into two parts, one of which may be derived from a potential. This latter portion will produce electrification and ultimately be counterbalanced by electric charges having a potential equal to $-\frac{1}{2}\mu\omega a\mathrm{I}\cos\phi\sin 2\theta/t$. The remaining portion of the electric forces will be

$$\Psi_{\mathrm{E}} = \quad \mu\omega\mathrm{I}\cos\theta\sin\phi/t, \quad . \quad . \quad . \quad . \quad (3)$$

$$\Psi_{\mathrm{S}} = -\mu\omega\mathrm{I}\cos\phi/t. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

These electric forces will tend to produce currents which are of the same type as those assumed to exist, but turned through a right angle in a direction opposed to that of the angular velocity. This is seen by comparing equations (1) and (2) with (3) and (4), and noting that the latter becomes proportional to the former when $\left(\phi+\frac{\pi}{2}\right)$ is substituted for ϕ. Hence the effect of these forces will be to add a system of currents which will have the same effect as a rotation of the original system in a direction opposite to that of the rotating sphere.

4. To show that the whole system of currents will rotate in the body and to determine the period of rotation some further calculations are necessary. The system of currents we are considering will produce a uniform magnetic field, M, within the sphere, which is equal to $\frac{8}{3}\pi\mathrm{I}$. The energy of the total magnetic field is easily found to be

$$\tfrac{1}{2}\mathrm{M}^2a^3 = \frac{32}{9}\pi^2\mathrm{I}^2a^3.$$

Now imagine such a system of currents as we have been considering, in which the current crossing an element ds_1 of the arc QA (fig. 1) is $\mathrm{I}\sin\alpha\, ds_1$, and let electric forces equal to $\mathrm{A}\sin\alpha$ act at each point on the system of currents. If ds_2 is an element of the line along which the forces act, the rate of doing work in the surface element $ds_1 ds_2$ is $\mathrm{AI}\sin^2\alpha\, ds_1 ds_2$. Hence the rate of doing work over the whole sphere is

$$\int \mathrm{AI}\sin^2\alpha\, ds_1\, ds_2 = 2\pi \mathrm{AI}a^2 \int_0^\pi \sin^3\alpha d\alpha$$
$$= \frac{8\pi}{3}\mathrm{AI}a^2.$$

The currents will increase in intensity and the rate of doing work must be equal to the rate of increase of energy. Hence, τ denoting time

$$\frac{32}{9}\pi^2 a^3 \frac{d}{d\tau}\mathrm{I}^2 = \frac{8\pi}{3}\mathrm{AI}a^2,$$

or

$$\frac{d\mathrm{I}}{d\tau} = \frac{3\mathrm{A}}{8\pi a}.$$

This equation will determine the rate of increase of the system of currents due to a given system of forces of corresponding type.

In the system of currents with OQ as axis, we may take the current-intensity I, at the points at which $\alpha = \frac{\pi}{2}$, to be the variable, which is now to be considered a function of the time τ. We also take I′ to be the corresponding variable of a system of similar currents having OR as axis. Introducing the forces due to the rotation of the sphere, we find that

$$\frac{d\mathrm{I}'}{d\tau} = \frac{3}{8\pi a t}\mu\omega \mathrm{I},$$

$$\frac{d\mathrm{I}}{d\tau} = -\frac{3}{8\pi a t}\mu\omega \mathrm{I}'.$$

From which we deduce

$$\mathrm{I} = \mathrm{I}_0 \cos \Omega\tau,$$

$$\mathrm{I}' = \mathrm{I}_0 \sin \Omega\tau,$$

where $\Omega = \frac{3}{8\pi}\frac{\mu\omega}{at}$, and I_0 is the initial value of I. Ω is the angular velocity with which the whole system of currents revolves.

5. The rate of rotation of a system of currents in a rotating spherical sheet which has been determined in the

simplest case, can also be calculated when the distribution of currents is of a more complicated character. Let there be a current function $a\Phi$ on a sphere of radius a from which the current-intensities are derived, so that if u_S and u_E are the currents in the direction of the axes of X and Y respectively:

$$u_S = a\frac{d\Phi}{dy},\quad u_E = -a\frac{d\Phi}{dx}.$$

Introducing polar coordinates and taking $dx = a d\theta$, $dy = a\sin\theta d\phi$, we find as in the previous paragraph that the electric forces Ψ_E and Ψ_S acting towards the south and east respectively are expressed by

$$\Psi_S = 2\mu\omega u_E \cos\theta / t$$
$$\Psi_E = -2\mu\omega u_S \cos\theta / t,$$

or

$$\Psi_S = -\frac{2\mu\omega\cos\theta}{t}\frac{d\Phi}{d\theta}, \quad \dots\dots (5)$$

$$\Psi_E = -\frac{2\mu\omega\cot\theta}{t}\frac{d\Phi}{d\phi}. \quad \dots\dots (6)$$

Put

$$\cos\theta\frac{d\Phi}{d\theta} = -\kappa\frac{d^2}{\sin\theta d\phi^2}\Phi + H, \quad \dots\dots (7)$$

and

$$\cot\theta\frac{d\Phi}{d\phi} = \kappa\frac{d^2}{d\theta d\phi}\Phi + K, \quad \dots\dots (8)$$

where κ is a constant and H and K functions of ϕ and θ, which are to be determined.

If an operation is performed with the equations (7) and (8) which may be represented by the symbol

$$\frac{d(7)}{d\phi} - \sin\theta\frac{d(8)}{d\theta},$$

the left-hand side of the resulting equation becomes

$$\frac{d}{d\phi}\cos\theta\frac{d\Phi}{d\theta} - \frac{d}{d\theta}\cos\theta\frac{d\Phi}{d\phi} = \sin\theta\frac{d\Phi}{d\phi};$$

on the right-hand side we have

$$-\kappa\left[\frac{d^3}{\sin\theta d\phi^3} + \frac{d}{d\theta}\sin\theta\frac{d^2}{d\theta d\phi}\right]\Phi + \frac{dH}{d\phi} - \frac{dK\sin\theta}{d\theta}$$

Hence

$$\frac{dH}{d\phi}-\frac{dK\sin\theta}{d\theta}=\kappa\sin\theta\frac{d}{d\phi}\left[\frac{d^2}{\sin^2\theta d\phi^2}+\frac{d}{\sin\theta d\theta}\sin\theta\frac{d}{d\theta}+\frac{1}{\kappa}\right]\Phi.$$

The right-hand side vanishes, if Φ is a surface harmonic of degree n, provided that $n(n+1)=1/\kappa$.

Hence we may put in that case,

$$H=\frac{dQ}{d\theta},\quad K=\frac{dQ}{\sin\theta d\phi}.$$

Equations (7) and (8) will now become

$$\Psi_S=\frac{2\mu\omega}{t}\left(\frac{1}{n\,.\,n+1}\frac{d^2}{\sin\theta d\phi^2}\Phi-\frac{dQ}{d\theta}\right), \quad . \quad . \quad (9)$$

$$\Psi_E=-\frac{2\mu\omega}{t}\left(\frac{1}{n\,.\,n+1}\frac{d^2}{d\theta d\phi}\Phi+\frac{dQ}{\sin\theta d\phi}\right). \quad (10)$$

As Φ only depends on ϕ in so far as it contains terms which have $\cos\sigma\phi$ or $\sin\sigma\phi$ as factors, the effect of differentiating with respect to ϕ is the same as a multiplication by σ and a change of $\sigma\phi$ to $\sigma\phi+\frac{\pi}{2}$. Hence the terms depending on Φ will be proportional to the original current-intensities if $\sigma\phi$ is replaced by $\sigma\phi+\frac{\pi}{2}$. In other words the currents which the forces Ψ_S and Ψ_E tend to produce are of the same type as the original currents, but turned through an angle $\frac{\pi}{2\sigma}$ round the axis of rotation, in a direction opposite to that of the angular velocity of the body. If the original current function has been proportional to $\cos\sigma\phi$ or to $\sin\sigma\phi$, inertia will tend to produce currents of the same type but proportional to $-\sin\sigma\phi$ or to $\cos\sigma\phi$ respectively. The final effect of these will be a rotation of the system of currents.

6. The terms depending on Q in (9) and (10) will not produce any permanent currents, but an electrification having $-2\mu\omega Qa/t$ for potential. We obtain Q from (8), by substituting $K=dQ/\sin\theta d\phi$. After integration with respect to ϕ, it is thus found that

$$Q=\Phi\cos\theta-\kappa\sin\theta\frac{d\Phi}{d\theta}.$$

This may be put into the standard form of tesseral harmonics, if we write

$$\Phi = \mathrm{T}_n^\sigma \cos \sigma\phi$$

and

$$\mathrm{T}_n^\sigma = \sin^\sigma\theta \, \frac{d^\sigma \mathrm{P}_n}{d\lambda^\sigma},$$

where $\lambda = \cos\theta$ and P_n stands for the zonal harmonic of degree n.

By differentiation we obtain

$$\sin\theta \frac{d}{d\theta} \mathrm{T}_n^\sigma = \sigma \cos\theta \, \mathrm{T}_n^\sigma - \sin\theta \, \mathrm{T}_n^{\sigma+1}.$$

We have also the following general equations :—

$$(2n+1) \sin\theta \mathrm{T}_n^{\sigma+1} = (n+\sigma+1)(n+\sigma)\mathrm{T}_{n-1}^\sigma - (n-\sigma+1)(n-\sigma)\mathrm{T}_{n+1}^\sigma ;$$

$$(2n+1)\mu \mathrm{T}_n^\sigma = (n-\sigma+1)\mathrm{T}_{n+1}^\sigma + (n+\sigma)\mathrm{T}_{n-1}^\sigma .$$

Combining these equations we obtain

$$n \, . \, n+1 \, . \, 2n+1 \mathrm{Q} = (n-\sigma+1) n^2 \mathrm{T}_{n+1}^\sigma \cos\sigma\phi + (n+1)^2 (n+\sigma) \mathrm{T}_{n-1}^\sigma \cos\sigma\phi.$$

7. To obtain the angular velocity of the system of currents, we may proceed as in the simple case, which has already been discussed.

A current-function $a\Phi_n$ of degree n produces a magnetic potential which inside the sphere is equal to

$$-\frac{n+1}{2n+1} 4\pi a \left(\frac{r}{a}\right)^n \Phi,$$

and in the outer space

$$\frac{n}{2n+1} 4\pi a \left(\frac{a}{r}\right)^{n+1} \Phi.$$

The energy of magnetic stress is easily calculated from this and found to be

$$4\pi a \frac{n \, . \, n+1}{2n+1} \int \Phi^2 d\mathrm{S}.$$

If there is a force-function Φ' from which the electric forces are derived in the same way as the currents from the current-function, the rate of doing work in a rectangular element bounded by the linear elements $ad\theta$ and $a \sin\theta d\phi$

will be

$$\left(\frac{d\Phi}{\sin\theta d\phi}\frac{d\Phi'}{\sin\theta d\phi}+\frac{d\Phi}{d\theta}\frac{d\Phi'}{d\theta}\right)dS.$$

But

$$\int\frac{d\Phi}{\sin\theta d\phi}\cdot\frac{d\Phi'}{\sin\theta d\phi}dS=\int\frac{\sigma^2}{\sin^2\theta}\Phi\Phi' dS,$$

as Φ and Φ' only contain ϕ in the form of a factor $\cos\sigma\phi$ or $\sin\sigma\phi$.

By partial integration, if again $\lambda=\cos\theta$,

$$\int_1^{+1}\sin^2\theta\frac{d\Phi}{d\lambda}\cdot\frac{d\Phi'}{d\lambda}d\lambda=-\int_{-1}^{+1}\Phi\frac{d}{d\lambda}\sin^2\theta\frac{d\Phi'}{d\lambda}d\lambda;$$

so that the total rate of doing work will be

$$\int\Phi\left\{\frac{\sigma^2}{\sin^2\theta}\Phi'-\frac{d}{d\lambda}\sin^2\theta\frac{d\Phi'}{d\lambda}\right\}dS,$$

which by the characteristic equation of tesseral harmonics becomes

$$n\,.\,n+1\int\Phi\Phi' dS.$$

The rate of doing work is equal to the rate of increase of energy; hence

$$\frac{8\pi a}{2n+1}\frac{d\Phi}{d\tau}=\Phi'. \quad \ldots\ldots \quad (11)$$

This equation connects the force-function Φ' with the corresponding current-function Φ.

Now let there be two current-functions, $a\Phi_1$ and $a\Phi_2$, both of degree n and differing only in so far as Φ_1 contains the factors $\cos\sigma\phi$, and a function of the time, and Φ_2 contains the factors $\sin\sigma\phi$, and some other function of the time.

The current-function $a\Phi_1$ will call forth a force-function $-\frac{2\mu\omega}{tn\,.\,n+1}a\Phi_1$ of the same type as Φ_2, and the current-function $a\Phi_2$ a force-function $\frac{2\mu\omega}{tn\,.\,n+1}a\Phi_2$ of the same type as Φ_1.

So that substituting in (11),

$$\frac{8\pi a}{2n+1}\frac{d\Phi_1}{d\tau}=\frac{2\mu\omega}{t}\cdot\frac{1}{n\,.\,n+1}\Phi_2,$$

$$\frac{8\pi a}{2n+1}\frac{d\Phi_2}{d\tau}=-\frac{2\mu\omega}{t}\cdot\frac{1}{n\,.\,n+1}\Phi_1.$$

It follows from this, that Φ_1 and Φ_2 are proportional to $\cos \Omega\tau$ and $-\sin \Omega\tau$ where

$$\Omega = \frac{\mu}{at} \cdot \frac{2n+1}{n \,.\, n+1} \cdot \frac{\omega}{8\pi}. \quad . \quad . \quad . \quad . \quad (12)$$

This gives the periodicity of the forces. The complete current-function will now be proportional to

$$\cos \sigma\phi \cos \Omega\tau - \sin \sigma\phi \sin \Omega\tau = \cos(\sigma\phi - \Omega\tau),$$
$$= \cos \sigma\left(\phi - \frac{\Omega\tau}{\sigma}\right);$$

so that the angular velocity with which the currents revolve is Ω/σ.

8. I have so far only dealt with electric currents confined to a spherical shell, as this problem adapts itself most easily to mathematical treatment. But in the simplest and most important case we may without difficulty obtain the solution for currents which circulate in the body of a conducting sphere. We take the case that the currents are such as would produce outside magnetic effects which can be represented by a magnetic potential of degree $-(n+1)$. Dividing the sphere into concentric shells we may neglect radial currents, and the currents within each shell may be represented by a current-function which is proportional to a surface harmonic of degree n. If we write $t\Phi$ instead of Φ in the previous investigation, the differential coefficients of this function will give current-densities instead of currents per unit linear cross-section, and we may apply equations (5) and (6), leaving t out of the denominator. The investigation of § 7 may be replaced by a simple application of a result given in Prof. Lamb's paper on electric currents in a sphere*. If electric currents are once started in a solid they will gradually die out owing to electric resistance, and if these currents are represented by a current-function, as assumed, the time-factor will be of the form $e^{-\lambda\tau}$, where the value of λ is given by Prof. Lamb for some of the simpler types of currents. The forces per unit volume which act on the currents under these circumstances are $-\rho i$, where i is the

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* Phil. Trans. 174, p. 519 (1888).

current-density and ρ the resistivity; the corresponding rate of diminution of current will be λi.

Hence if Φ represents the current-function and Φ' the corresponding force-function, we may put $\Phi' = -\rho i$ and $\frac{d\Phi}{d\tau} = -\lambda i$, and derive

$$\frac{d\Phi}{d\tau} = \frac{\lambda}{\rho}\Phi'.$$

This shows that in equation (12) we must replace $\frac{2n+1}{8\pi a t}$ by $\frac{\lambda}{\rho}$. The angular velocity of the rotating currents then becomes

$$\frac{\Omega}{\sigma} = \frac{\mu\omega}{n\,.\,n+1}\cdot\frac{\lambda}{\rho\sigma}.$$

For $n=1$, we have for the simplest case $\lambda^{-1} = \frac{4}{\pi}\frac{a^2}{\rho}$, so that

$$\Omega = \frac{\mu\pi}{2a^2}\omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

9. We may now apply the results obtained to the case of electric currents which we may imagine to circulate in the earth. If terrestrial magnetism is due to such currents, we may represent them by a superposition of different systems, each system producing magnetic forces on the outside, the potential of which is represented by a spherical harmonic. As regards the currents which give rise to zonal harmonics, they must flow in circles at right angles to the axis of rotation and the revolution of the earth cannot affect them. The tesseral harmonics will revolve relatively to the earth in a direction opposite to that of its own rotation. The effects are therefore such as are actually observed. But the calculated angular velocity is much too small to explain the secular variation.

Taking the case of a solid sphere first. If $\mu=1$, which is a possible case if the conductivity is of an electrolytic character,

$$\Omega = \frac{\pi}{2a^2}\omega = \frac{\pi}{8\times 10^{17}}\omega.$$

Hence the time of revolution of the magnetic system would be $2{\cdot}5\times 10^{17}$ days or about 7×10^{14} years. No admissible value of μ could reduce this number very materially. If the currents could be imagined to be confined to a sheet of thickness t, the angular velocity would be increased to

$$\Omega = \frac{3}{8\pi} \frac{\mu}{at} \omega.$$

Taking $\mu/t = 1$ this would give for the period of revolution $8\pi a/3$ or as $2\pi a = 4 \times 10^9$ the periodic time would be 5×10^9 days, or 14×10^6 years, which is still of a much bigger order of magnitude than the period of the secular variation. To produce a revolution of the magnetic system of *e.g.* 500 years t/μ would have to be equal to 36×10^{-6}, so that for possible values of μ, t would have to be reduced to molecular dimensions.

10. The fact that a current sheet of molecular dimensions would show a magnetic precession of angular velocity comparable with that of the secular variation suggests the possibility of the phenomenon being rather of a molecular than a molar character. If terrestrial magnetism is due to the rotation of the electron round the atom, a precession of the required amount might be produced. But the subject is not capable of theoretical treatment without making some assumptions of too speculative a character to be introduced here.

An experimental investigation would be more likely to help, for it might give an answer to the question :—" Does the magnetic axis of a transversely magnetized sphere or of a steel disk magnetized along a diameter, lag behind when the sphere or disk is rotating rapidly ? " Some trials which were made, under not very suitable conditions, have given me a negative answer to the question, but I hope to be able to arrange for more decisive experiments.

11. In the above investigation it has been assumed that electric currents are conveyed equally by the two opposite electricities, so that the current as a whole has no moment of momentum, but as far as I can see without detailed calculation the general result of the investigation would not be altered, even assuming the existence of angular momentum. As far as the results of this investigation are concerned, we must conclude that the inertia of electric currents, which doubtless does exist, is too small to account for the observed secular variation of terrestrial magnetism.

DISCUSSION.

Prof. RÜCKER congratulated the author upon his attempt to solve the problem of terrestrial magnetism, and expressed the hope that further calculation would throw more light upon this difficult subject.

Mr. BLAKESLEY asked if the time of the secular variation would be altered if the interior of the earth were liquid or solid.

Prof. LODGE observed that the precession was rapid in the case of a thin enough layer, and mentioned J. J. Thomson's notion that the electrons were thrown out by centrifugal force, and formed a layer of molecular thinness. Hertz, in his experiments on electricity, had looked for material inertia besides electromagnetic inertia. In the present theory the distinction disappears, and there is only one inertia, and that electromagnetic, though not in the ordinary sense as contributing to self-induction.

Prof. AYRTON said if the two forms of inertia were electromagnetic, he would like to know why in detecting the second form it was necessary to associate it with an absorption of energy as in the case of an electrodeless discharge. In the case of ordinary self-induction there is no absorption of energy, and if there is absorption in the second form, and if they are both electromagnetic, he would like to know the difference between the two.

Prof. SCHUSTER, replying to Mr. Blakesley, said that if the interior of the earth were treated as liquid, the period of the cycle would be about one hundred times less. In reply to Prof. Ayrton, he said he had only cited one experiment to show that a phenomenon explained by the gas being a good conductor could also be explained by its electric inertia. It was impossible to say in general whether self-induction caused an absorption of energy or not.

XLV. *The Anomalous Dispersion of Carbon.*

By Prof. R. W. Wood [*].

It was suggested to me some time ago by Professor Ames that the rapid decrease of amplitude on a wave-front, resulting from its passage through a prism of some strongly absorbing substance, such as cyanine, might not be without influence on the direction of propagation of the transmitted ray.

In Huygens's construction a constant amplitude is assumed over the wave-front, and it is quite conceivable that varying the amplitude might shift slightly the position of the "effective-point."

There are obviously two ways of attacking the problem: the mathematical and the experimental. I have been unable to treat the case by any of the geometrical methods, and the simplest way seems to be to determine the form and position of the intensity curve, treating the transmitting edge of the prism as a narrow aperture, the amplitude decreasing across its width according to some linear function, and solving by the method employed in the case of the Fraunhofer or telescopic diffraction phenomena. I have not yet attempted the solution in full, but a cursory examination leads me to anticipate that the central maximum will not be symmetrical with respect to the centre of the system. The highest point of the intensity curve will undoubtedly be at its usual place, in the line normal to the centre of the aperture, but the slope may be steeper on one side than on the other. In all determinations of the refractive index of strongly absorbing prisms, when working near the absorption-band, the slit image is broadened by diffraction. By setting the cross-hair of the eyepiece on the centre of this broadened image, we assume that we have determined the centre of the system. If, however, the central maximum of the pattern is unsymmetrical, it is clear that a considerable error may be introduced in this way.

For a direct experimental test we require some means of cutting down the amplitude without introducing a retardation or change of phase. In searching for a possible substance which would absorb but not retard, I tried films of smoke on glass. It seemed possible that, since the absorption is caused by very minute opaque particles of carbon, the wave might be transmitted without retardation. If this were found to be the case, a wedge-shaped film of smoke would furnish the necessary conditions. Examination of the films by means of the interferometer showed, however, that a very marked retardation was introduced. This phenomenon I subsequently found had been previously observed by Rosicky * and Stark †.

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[*] Read November 23, 1900.

Stark's results indicated that in the case of films deposited by coal-gas flames, we are dealing with a porous mass consisting of 2·28 per cent. of pure carbon, and 97·72 per cent. of air. He considered the case as that of a turbid medium made up of air with a low, and carbon with a high refractive index, such mixtures being known to possess a refractive index intermediate between the indices of the constituent parts. He made no determinations of the dispersion.

It occurred to me that the retardation in this case might be ascribed to diffraction, there being an increase of path due to the passage of the light waves around the carbon particles, the case being analogous to the passage of a sound-wave through a medium containing obstacles symmetrically distributed. I succeeded in photographing the retardation of a sound-wave resulting from its passage through several layers of glass tubes, placed side by side with spaces between. If the retardation of the light by carbon films is due to diffraction, we should expect either to find dispersion absent, which would mean that the path increase is the same for all waves, or else a greater retardation for the long waves than for the short.

An attempt was at once made to determine the presence or absence of dispersion, the experiments showing conclusively that the long waves (red) were retarded more than the short ones (violet), the condition found *within* the absorption-band in the case of substances showing anomalous dispersion.

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* Rosicky, *Sitzb. Ber. Wien. Ak.* 1878.

† Stark, Wied. *Ann.* lxii. p. 351.

Experiments were made with smoke-films, and with films deposited in a vacuum on plate-glass by the filament of an incandescent lamp. The average diameter of the carbon particles in smoke-films is less than 0·00026 mm., while the regular reflexion at normal incidence of violet light by the deposited films indicates that the diameter of the particles must be less than one-eighth of the wave-length of violet light. (Assuming $\frac{1}{4}\lambda$ to be the maximum allowable phase-discrepancy.)

The dispersion was first measured with a Michelson interferometer, illuminated with monochromatic light of various colours obtained by prismatic analysis. The fringes were photographed and measured as described in the paper on Cyanine *, readings being obtained between wave-lengths ·00040 and ·00066. The results showed a steady increase of refractive index in passing from blue to red. The results obtained with the deposited films were less satisfactory, owing to the poor quality of glass. They were prepared in the following way:—An incandescent lamp bulb was cut in two and a small piece of German plate-glass introduced; the two halves of the bulb were then sealed together in the blowpipe flame, and the air exhausted, after which the lamp was run for several hours at considerably above its rated candle-power. Very uniform metallic-like films were obtained in this way, which gave elliptic polarization. The poorness of the glass, however, made accurate measurements impossible, owing to the irregular curvature of the fringes, and the work will be repeated with films deposited on plane-parallel optical glass. This seems to be important, since it seems quite possible that the films may be molecular in structure; the particles are certainly much smaller than in the case of the smoke-films, and may give a different dispersion curve. As far as it was possible to judge the deposited films showed the same anomaly as the smoke-films.

No attempt was made to determine the absolute refractive index, since accurate determinations of the thickness of the smoke-films are difficult. Even were this possible the values

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* "The Anomalous Dispersion of Cyanine," R. W. Wood and C. E. Magnusson, Proc. Phys. Soc. *antè*, p. 542.

obtained would not mean much. Relative values only were obtained, as indicated in the following table, where n represents the fringe displacement, *measured in fringe-widths*, λ the wave-length, and $n\lambda$ the product which is proportional to the refractive index, as shown by the usual formula

$$(\mu-1)e=n\lambda,$$

where e is the thickness of the film.

Smoke-Film.

n.	λ.	$n\lambda$.
·853	663	566
·923	605	558
·960	566	543
1·037	520	539
1·064	479	510
1·124	436	490
1·149	414	476

In the case of the films deposited by the lamp, which do not have the exceedingly porous structure of the smoke-films, we can easily determine the thickness by substituting the half-coated plate for the back mirror of the interferometer, and measuring the shift of the fringes at the edge of the reflecting carbon-film. A displacement of one third of a fringe was found with sodium light. The thickness was therefore $\frac{1}{2}\times\frac{1}{3}\times{}$·000589 or ·000098 mm. The displacement of the sodium-light fringes corresponding to four transmissions (two films in optical juxtaposition being used as described in the paper on cyanine) was 0·784 of a fringe, or 0·196 for one transmission. We have then, substituting in the formula

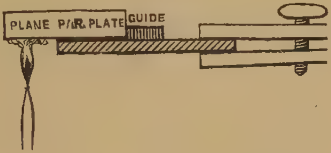
$$(\mu-1)\cdot000098=\cdot196\times\cdot000589$$

$$\mu-1=1\cdot2,$$

or the refractive index $\mu=2\cdot2$, not very far from that of the diamond.

One instinctively places more reliance on determinations of refractive index made by prismatic deviation than on those based on interference methods, and an attempt was accordingly made to verify the results with carbon prisms. By arranging a very small pointed gas-flame close to the edge of a glass plate, and sliding a piece of plane parallel optical glass back and forth against a guide (the tip of the flame just touching it), very uniform prismatic deposits of smoke were secured. Viewed in reflected light the films showed Newton's interference colours, and the prisms were judged by observing whether the coloured bands were straight and properly spaced.

Fig. 1.



Formation of smoke-prisms.

A suitable prism having been selected, the plate was covered with a piece of black paper perforated with two rectangular openings of equal width.

One of these openings, which was several times higher than the other, was over the prism, while the other covered clear glass close to the refracting edge of the prism. The object of using diaphragms of the same width but of different heights was to secure similarity of the deviated and undeviated images of the slit. The width of the central maximum depending on the width of the opening alone, the height could be increased to allow the passage of more light in the case of the dark prism.

The plate was then placed in a large direct-vision spectroscope (from which the prisms had been removed) and the slit illuminated alternately with red and blue light. A very intense light being necessary the electric arc was used, the slit being covered alternately with deep ruby glass and a glass trough containing a strong solution of cuprammonium combined with a cyanine film. Prismatic analysis was found to weaken the light too much.

The diaphragms were covered alternately, and readings taken of the position of the slit image with a filar micrometer.

The following readings were obtained :—

Red.	Blue.
Distance between dev. and undev. image in divisions of micrometer.	Distance between dev. and undev. image in divisions of micrometer.
55	40
60	50
59	41
58	48
57	45
58	46
53	43
56	39
55	44
61	40
57·2 mean.	43·6 mean.

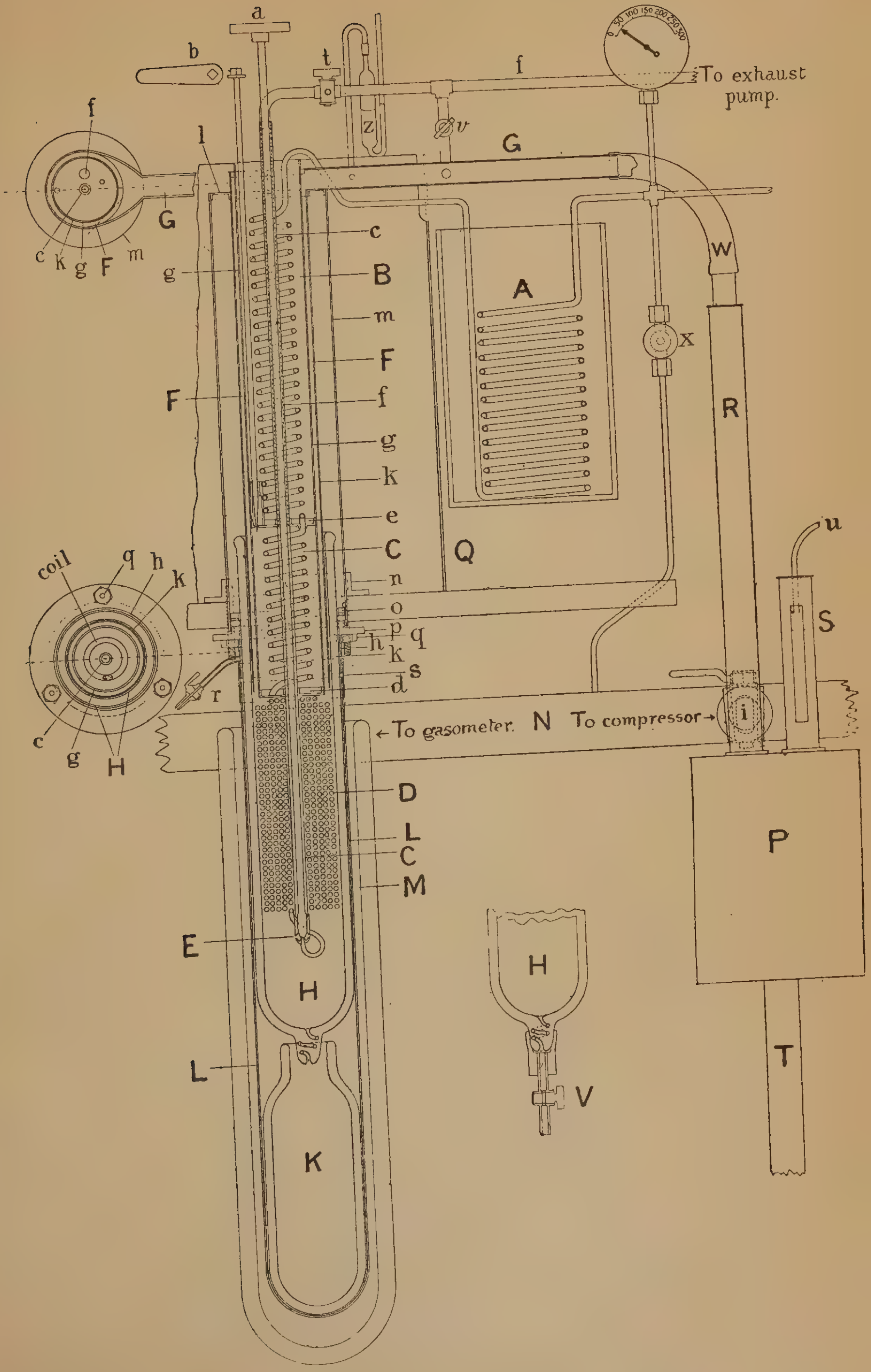
In order to see how these readings agreed with the deviation calculated from an interferometer determination of the retardation at the base of the prism, the plate was set up in front of one of the mirrors of the instrument, a plate of equal thickness being introduced in the other optical path as a compensator. The fringes sloped abruptly down across the face of the prism, the displacement at the base being 1·7 of a fringe for the double transit of Na light, or ·85 for a single passage. The retardation is therefore ·00059 × ·85 or ·0005015 mm. The width of the prism was 2·24 mm., therefore the angle through which the wave-front should be turned is given by

$$\tan\theta = \frac{\cdot 0005105}{2\cdot 24}$$

$$\theta = 46''.$$

The actual deviation as observed in the spectroscope was determined as follows :—

Calibration of the filar micrometer showed that one complete revolution of the head (100 divisions) corresponded to ·248 mm.; 50 divisions, the mean between red and blue


a
b
t
f
0 50 100 150 200 250 300
To exhaust pump.
z
v
G
f
l
G
c
k
g
F
m
g
c
B
m
F
f
g
k
e
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A
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Q
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q
h
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coil
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h
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c
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S
To gasometer.
N
To compressor
i
D
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H
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T

corresponding approximately to the deviation for sodium light, represents a shift of ·124 mm.

The focal length of the telescope was 600 mm., and the deviation is given by

$$\tan \theta = \frac{\cdot 124}{600}$$

$$\theta = 43'',$$

which agrees very well with the calculated deviation of 46″.

While the results obtained are what we should expect if the diffraction theory were true, they do not of course prove it; and it will not be safe to draw deductions until more accurate results have been obtained with the metallic deposits obtained from the incandescent carbon filament. A method of compensation has been devised, which will make observations with much thicker films possible.

In conclusion I must thank Dr. C. E. Magnusson for much valuable assistance in photographing and measuring the fringes.

Physical Laboratory of the University of
Wisconsin, Madison.

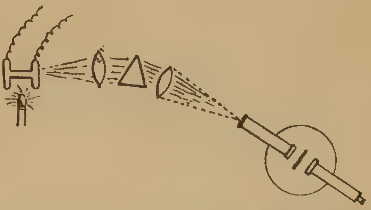
XLVI. *A Mica Echelon Grating.*

By Prof. R. W. Wood*.

Having experienced some difficulty, when discussing Michelson's remarkable retardation-grating, in making students understand how it is possible for the sodium lines to be separated by a distance fifteen or twenty times as great as the distance between the spectra, it struck me that an echelon, built up of very thin films instead of thick plates, coming midway between the ordinary grating and the echelon as commonly constructed, would be useful in demonstrating the theory.

Such a grating I have made of mica.

By it lines, which with an ordinary grating of the same number of grooves would appear single, can be resolved and still not be farther apart than the spectra. It shows spectra of the same general appearance as in the more powerful instruments, can be set for single and double order, and though useless as a tool for research, is almost as satisfactory for purposes of demonstration as the costly batteries of thick plates.



A number of thin sheets of mica were examined with the interferometer, and one selected over a considerable portion of which the fringes appeared straight and unbroken. This area was roughly outlined with a pin-scratch, and cut up into a dozen small rectangles with a print-trimmer. The retardation of one of these was measured with the interferometer, and found to be fifty wave-lengths for sodium-light. The grating would therefore yield spectra of about the 50th order: I say "about," for the order varies with the wave-length of the light and the inclination of the grating. A grating-space of 0·5 mm. was determined upon, and a strip of glass was accordingly ruled with this spacing on a dividing-engine. On this scale the echelon was built up, the plates being put in position under the microscope, and cemented at the edges by means of small bits of sealing-wax and a hot wire.

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* Read February 8, 1901.

Considerable difficulty was found in attaching each plate without disturbing the spacing of the others. The first two or three gratings that were made were not very satisfactory; but some experience having been obtained by practice, an excellent one was finally obtained. Only nine plates were used owing to the opacity of the mica in thicker layers. The battery was mounted on a square of cardboard over a rectangular opening of the same size, a clear space 0·5 mm. wide being left to serve as the first grating-line of zero retardation. The whole number of lines was therefore ten.

The resolving-power, represented by the product of the number of lines and the order of the spectrum, would accordingly be about 500. Obviously the sodium lines, requiring a product of at least 1000 for resolution, were beyond the power of the instrument; but the two yellow mercury lines, separated by 2·5 times the distance between the Na lines and requiring a product of only 280, seemed suitable.

The light from an "end-on" mercury-tube, after passing through a collimating-lens and prism, was focussed on the collimator of a spectrometer, the green (monochromatic) image of the tube being brought on the slit. On placing the echelon on the table of the instrument the spectra showed clear and sharp, and by turning the grating a little could be brought into either single or double position (see Lord Blythswood and Dr. Marchant's paper, Phil. Mag. Apr. 1900). Faint secondary maxima appeared between the principal maxima, owing to the small number of grating elements.

By slightly shifting the position of the lens, the yellow light from the tube was now focussed on the slit, when the principal maxima immediately doubled in a most beautiful manner and the faint secondary maxima disappeared owing to overlapping. The distance between the components was about one third of the distance between the spectra. For the sake of comparison, a grating of the same spacing and number of lines was ruled on a piece of smoked glass. (To prevent the film from tearing it should be first wetted with alcohol and dried.)

The slit was illuminated with white light, and a cyanine film placed before it. This cut off all but the extreme red and blue; and it was found that in the first order the grating was unable to separate the extreme red and blue of the spectrum, while the echelon easily resolved the Hg lines, showing the effect of the introduction of retardation.

The constants of the grating were as follows :—

t the Thickness of plates 0·05 mm.
Width of space 0·5 mm.
Retardation of each plate, 50 waves.

Calculating the separation of the Hg lines by Michelson's formula, we have

$$\frac{\delta\theta}{\delta\theta_1} = \frac{t}{\lambda} \cdot \frac{\delta\lambda}{\lambda}, \quad \text{where } t = 0{\cdot}05 \text{ mm.}$$

$$\frac{t}{\lambda} = 94,$$

$$\frac{\delta\lambda}{\lambda} = 280,$$

$$\delta\theta = \delta\theta_1 \frac{94}{280} = \frac{1}{3};$$

or the distance between the Hg lines is $\frac{1}{3}$ of the distance between the spectra.

It will be found instructive to illuminate the slit-plate of the spectrometer with a focussed continuous spectrum, and observe the way the different orders of echelon spectra file by when the continuous spectrum is moved across the slit, showing the dependence of order on wave-length.

If the slit be illuminated with white light and a continuous spectrum be formed in the telescope by means of a prism, this spectrum will be found to be crossed by heavy dark bands when the echelon is placed in front of the prism. The explanation of these bands makes a good problem for advanced students. A clew may be found by repeating the experiment with the slit-plate illuminated with the continuous spectrum instead of white light, and moving this spectrum very slowly.

It may be of interest to some to know that the Zeeman effect can be shown with an echelon made of four interferometer-plates, the light being the green rays from a mercury tube.

Physical Laboratory of the
University of Wisconsin, Madison.

XLVII. *On the Propagation of Cusped Waves and their Relation to the Primary and Secondary Focal Lines. By* Prof. R. W. Wood*.

In a previous paper† I have shown the forms of the wave-fronts reflected from spherical surfaces, by means of geometrical constructions, and photographs of the actual waves. In the present paper I shall discuss somewhat more fully the case of the reflexion of a plane wave by a hemispherical mirror, where we have a reflected wave of a form which I have likened to a volcanic cone. A superficial examination of the forms might lead one to imagine that the bowl of the crater collapsed to a point at the principal focus of the mirror. This can of course only be true in the case of a concave spherical wave, which is only given by a parabolic mirror. We shall find as a matter of fact, if we examine the geometrical construction, that the cusp of the wave, or the rim of the crater, which traces the caustic as I have shown, is continuously passing through a focus. In other words, the curvature of the crater increases as we go from the bottom to the rim, at which point the radius becomes zero. The inner edge is then continually passing through a focus and appearing on the outside, building up, as it were, the sides of the cone. These wave-fronts were drawn by constructing the orthogonal surface, which was shown to be in section an epicycloid formed by rolling a circle whose diameter was equal to the radius of curvature of the mirror, around the outside of the mirror. The evolute of this curve is the caustic, itself an epicycloid, and the reflected wave-fronts form a family of parallel curves, which are the involutes of the caustic.

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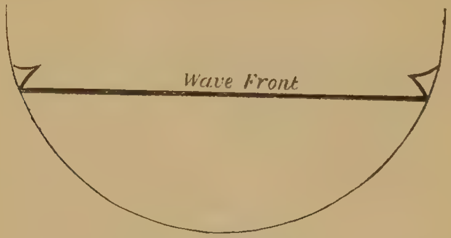
* Read February 22, 1901.

† Phil. Mag. July 1900, p. 148.

Though the caustic and orthogonal surface (evolute and involute) are similar epicycloids, the reflected wave-fronts, or parallels to the orthogonal surface, are not epicycloids. It may be well to point out here an error that sometimes appears in text-books on Optics, namely, the assumption that the wave-front (say in the case of a spherical wave refracted at a plane surface) is an hyperboloid in the second medium, because the caustic is the evolute of an hyperboloid. An hyperboloid wave will not propagate itself as an hyperboloid, nor an ellipsoidal wave as an ellipsoid (except in an anisotropic medium), the parallels to a conic being in general curves of the eighth degree. In the case above cited, we should speak of the wave-fronts after refraction as the parallels to an hyperboloid.

Fig. 1.



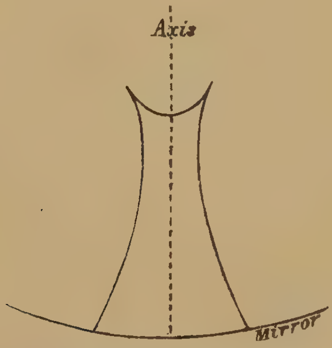
Let us suppose the wave to be just entering the mirror. The form of the portion which has already suffered reflexion is a cusp extending around the upper edge of the hemisphere (fig. 1). The upper branch of the cusp is concave upward, and is the portion of the wave which left the reflecting surface first and has passed through a focus. The lower branch is concave downward, or in the direction of propagation, and represents the portion of the wave which has just left the surface and is on the way to its focus. The radius of curvature increases from zero as we go away from the cusp-point along either branch, as I have said before. This cusped wave moves down the mirror, the lower branch being continually replenished by consecutive portions of the incident wave as it encounters the mirror, the upper branch being continually added to by elements of the lower branch as they pass through their foci at the cusp.

As I have said in a previous paper, the cusp traces the caustic surface; and since the wave is always coming to a focus on the cusp, the increased illumination along the caustic is accounted for.

Let us now examine the relation of these reflected wave-fronts to the primary and secondary focal lines. If we inspect the diagram usually given to illustrate the formation of focal lines (Winkelmann, p. 33, for example), it is at once apparent that the wave-front between the two focal lines is expanding along one meridian, and contracting along a meridian at right angles to it; in other words, the wave is convex along one meridian and concave along the other. The form of the surface is not unlike a small bit on the inside of an anchor-ring.

Consider now the diagram shown in fig. 2, remembering that the complete wave-front at this stage is formed by the rotation of this figure around the axis of the mirror. The bowl of the crater is concave along every meridian, but it is at once apparent that any portion of the outer slope has the required saddle-shape, being concave in horizontal planes and convex in vertical planes. From this it is evident that the outer wall of the volcanic cone, before it crosses the axis of the mirror, always represents the portions of the wave-front between the primary and secondary focal lines.

Fig. 2.

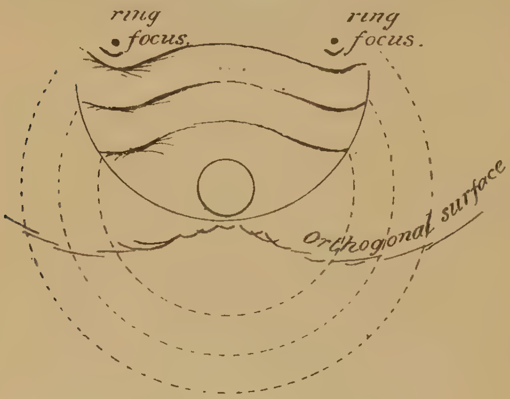


That this is true is evident, when we recollect that the first focal line is formed by the intersection of rays on the caustic surface, or, regarded from the wave point of view, by the passage through their foci on the cusp of the wave of adjacent elements of the wave-front. The second focal line lies on the axis of the mirror; consequently the wave-front between the lines is that portion of the surface which has passed through a focus on the cusp, but which has not crossed the axis.

I have found that a small glass model of the wave-front, shown in cross section in fig. 2, is extremely useful in making the whole matter clear. It can be made by drawing down a large thin tube, melting the end down flat, and then sucking it in a little.

Another useful piece of apparatus can be made by silvering the outside of a hemispherical glass evaporating-dish or half of a large round-bottomed flask. The concave mirror thus formed should be mounted on a stand, and a two-candle power "pea" electric lamp arranged so that it can be moved along the axis of the mirror. In my second paper on the photography of sound-waves it was shown that a spherical wave, starting in the principal focus of a hemispherical mirror, is reflected as a saucer-shaped wave, the curved sides of the saucer coming to a focus in a ring surrounding the nearly flat circular bottom. If we place the lamp in the focus of the

Fig. 3.



mirror, and hold a sheet of ground-glass in front of it at the proper distance, we can show the luminous ring and the uniformly illuminated circular area within it. If we move the lamp to a point midway between the principal focus and the surface of the mirror, we get a ring of intense brilliancy, with but very little light within it.

The wave-front constructions for this condition are shown in fig. 3, the distribution of energy being roughly shown by shading the reflected wave-fronts.

While I have brought out nothing but what would be apparent to anyone on a very cursory examination of the constructions, some of the points may be of use to those engaged in teaching elementary optics.

University of Wisconsin.

XLVIII. *On Cyanine Prisms and a New Method of exhibiting Anomalous Dispersion. By* Prof. R. W. Wood.[*]

I have already described a method of making prisms of solid cyanine by pressing the fused dye between plates of glass, which are far superior to liquid prisms or the solid prisms made by Wernicke for the purpose of exhibiting anomalous dispersion.

Until quite recently I considered that twenty or thirty minutes was about as large an angle as could be used to advantage. With such large angles very little green light gets through the prism, and on viewing a source of light through the refracting edge we see merely a red and a blue image, the former being deviated more than the latter. With a new supply of the dye which we have just received I have, however, been able to make prisms of over one degree, which transmit an abundance of green light. Viewing the incandescent loop of an electric lamp through one of these prisms, we see a most beautiful anomalous spectrum—a broad band of light with the colours arranged in the order green, blue, violet, red, and orange. When it is remembered that the largest angle which Pflüger was able to obtain by Wernicke's method was of but two minutes, the advantage of the fusion-method is apparent.

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[*] Read February 22, 1901.

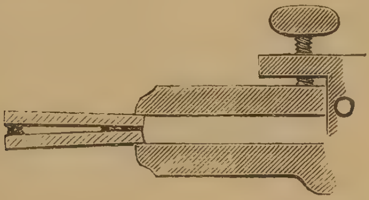
While engaged in some experiments on the dispersion of selenium, from which most beautiful prisms can be made by the same method, I was led to try the experiment of crossing one of these prisms with a small diffraction-grating. Selenium has an extraordinarily high refractive index, over 3 for certain colours, and the prisms are quite transparent for the red and orange. The deviation produced by one of these prisms is about double the angle of the prism, and I was led to try the experiment of crossing one of them with a diffraction-grating. On viewing an arc-lamp through the combination, the diffraction-spectra were most distinctly seen on each side of the central image, each one with its tail nicely curled up at the edge of the absorption-band, which begins in the yellow and stretches to the extreme ultra-violet.

Having such excellent cyanine prisms at my disposal, it occurred to me to try crossing one of these with a diffraction-grating, for the purpose of showing the dispersion-curve. I have usually used a spectrometer and low-dispersion prism for this purpose. The grating mounted with the cyanine prism was found to be equally efficient. One has only to view an arc-light through the combination. The diffraction-spectra are deviated by the prism, the red ends being turned up, while the blue-green ends are turned down in a most beautiful manner. I used a photographic copy of a 2000-line-to-the-inch grating, about 5 mm. square, fastened over the refracting edge with sealing-wax.

The curved spectra can also be seen when the sun is viewed through the combination, though less perfectly, owing to its size.

In conclusion, some hints regarding the construction of cyanine prisms may be of use to any wishing to repeat the experiment.

The cyanine was obtained from Grübler of Leipzig, and is in the form of lumps of quite minute crystals. The old sample had a different appearance, consisting of long needle-shaped crystals not caked together. A certain amount of dexterity is required to make good prisms, which can only be acquired by practice. Small rectangular pieces of thin German plate glass are prepared (measuring about 2 × 3 cm.), and a thin strip cut from a visiting-card glued along the short side of one. A piece of cyanine about the size of a coarse shot is placed near the opposite side, and the edge of the plate heated over a small flame until the dye fuses, holding another cover-strip in the flame at the same time, in order to have both at about the same temperature. The hot edge of the cover is now to be brought down into the cyanine, and the plate gently lowered until the edge rests on the strip of card. The plates must be at once placed under pressure in a small clamp, where they are to remain until cold. I find that the flat-jawed metal clamp of one of Gaertner's laboratory supports gives the best results. The pressure is to be applied close to the refracting edge of the prism only, as shown in the figure. This is very important. Experience is the only guide to the degree of pressure required. With the new sample of cyanine the removal of one of the glass plates, when this is desired, is much easier than with the old. For most purposes, however, I prefer to leave the cover on, cementing the two plates together with sealing-wax.



It will be found that there is a very narrow strip of clear glass at the refracting edge, where the glass plates have come into optical contact. This produces a diffraction-band superposed on the anomalous spectrum, but it is so faint that it is not troublesome.

It is usually necessary to turn the prism slightly to get the green part of the spectrum; that is, the incidence should not be normal. (Examples exhibited.) The cyanine prism should be held with the label-side towards the eye, and an incandescent lamp or gas-flame turned edgewise viewed through the slit. The refracting edge (which is to the left) should be turned away from the eye a little, though the eye must be brought close up to the aperture. The same thing applies when using the prism in connexion with the spectrometer.

To see the dispersion curve by means of the grating and prism, one has only to view a naked arc-lamp through the small rectangular aperture.

University of Wisconsin.

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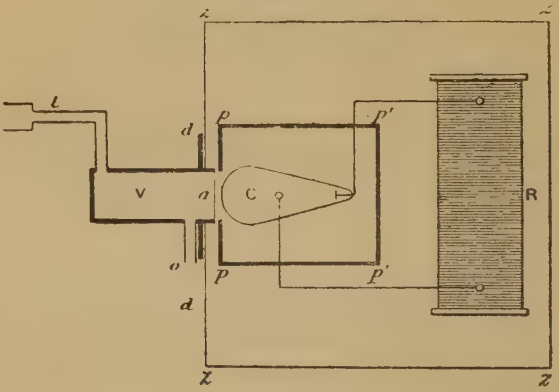
XLIX. *How Air subjected to X-rays loses its Discharging Property, and how it produces Electricity.* *By* Prof. Emilio Villari (Honorary Fellow of the Physical Society) [*].

The apparatus used in my experiments is indicated by the figure here adjoined.

A Crookes's tube C (fig. 1), enclosed in a small lead case $p\,p'$ with thick walls, was excited by a powerful inductorium

Fig. 1.



R, which, along with the small case $p\,p'$, was enclosed in a large case of zinc $z\,z'$, connected to earth by means of the gas-pipes.

The walls of the cases opposite to the anticathode had two large openings through which there entered a vessel V quite close to the Crookes's tube. This vessel, of cylindrical form (30 centimetres by 11), was made of a thick sheet of lead, with the exception of its base *a*, turned towards C, which was formed of a thin leaf of aluminium. Two tubes, *o* and *t*, served, with the aid of a constant-pressure bellows, to drive a current of air across the vessel V. A large sheet of lead *d* soldered to the vessel hindered the radiations from escaping; and for the same purpose the tube *t* was formed with an elbow. The air which had been rendered active by the X-rays in the vessel V passed out through tubes joined on at *t* and was directed against one of my electroscopes, having a single gold leaf, protected by a metallic box connected to the earth. The gold leaf, by means of two slits cut in the walls of the box and closed by a metallic gauze, was illuminated by a glow-lamp and observed by means of a telescope having a divided-scale micrometer.

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[*] Read February 22, 1901.

Air made active by X-rays, in the vessel V, in passing through a long tube, coiled in many turns, loses much more of its discharging power than it does in passing through the same tube if straight. The experiments were executed with tubes of copper, lead, glass, and caoutchouc. The material of the tubes does not influence the phenomena.

The air which has been made active with X-rays loses a great part of its discharging properties, by streaming upon pencils, or rather bundles, of many long and flexible wires of brass contained in surrounding tubes of glass or metal.

A flexible tube of copper 3 metres or more in length and 1 centimetre in diameter, coiled in 8 or 10 turns, and well insulated with paraffin and with a stem of glass, charges itself to a positive potential of about 30 volts when it is traversed by active air*. It is necessary to insulate the copper tube from the rest of the apparatus, not only with the paraffin, but also with a glass tube of 30 to 40 centimetres in length, to lessen the discharge of the tube of copper, as happens through convection, by means of the same active air.

Filters made with brass tubes (10 × 2·5 centimetres) closed with 30 to 60 disks of strong gauze of brass, copper, or aluminium, when traversed by a current of active air, take a positive charge to a potential of 15 volts, increasing a little with the number of the disks, and perhaps with the fineness of the meshes of the gauze adopted.

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* To avoid repetition the term "active" air is here used for air which has been rendered active by being exposed to X-rays. The term used by Prof. Villari is "aria ixata." [TRANSL.]

Square pieces of not very fine gauze of brass, 20 to 25 or more centimetres in the side, rolled and wrapped round themselves, and introduced into suitable tubes of glass or of metal, take positive charges from 15 to 20 volts when they are traversed by a current of active air.

Some metallic leaves equal in size to the pieces of gauze, and rolled up in a similar manner, all took from the current of active air negative charges with a potential of about 10 volts. The experiments were made with leaves of copper, iron, zinc, brass, tinned iron, platinum, aluminium, and tin. The charges varied principally with the way in which the leaves were rolled up.

Strips of the metals mentioned, 51 centimetres long by 2·7 centimetres broad, introduced into a tube of glass or metal and subjected to streams of active air, charged themselves at least to a potential of 3 to 5 or more volts. The strip of polished aluminium often took a lesser charge than the others. The strips of gauze equal in size to those of sheet metal took negative charges, similar, but sensibly superior to those assumed by the sheet metal strips.

Finally, the closed tubes and the brass wires introduced into tubes of glass or metal charged themselves negatively when they were subjected to streams of active air.

It seems that the metals, independently of their nature, take a positive or a negative charge according to whether the active air rubs against them with force or lightly; and this result is confirmed by the following experiments.

Tubes of copper or of lead, if short, and particularly if straight, traversed by active air take a negative charge; but if long, and particularly if coiled upon themselves, take positive charges which may attain sufficiently high potentials.

Coarse turnings of copper well rammed into a tube of glass or metal take a positive charge from active air; but if inserted in small quantity and sparsely, they take a negative charge.

Cylinders of diverse sizes, made with leaves of gauze of a moderate breadth, put into tubes of glass or metal traversed by active air, take positive charges if they are long, and negative if they are short. In my researches the positive charges grew with the length of the cartouches, beginning at about 15 centimetres; and the negative grew with a diminution of the length of the same from about 12 centimetres down to 2 centimetres.

Ribbons of gauze 2 centimetres wide and of various lengths (from 20 to 60 centimetres), rolled up into a cylinder two centimetres high, and placed in a tube of glass or brass, took a positive or a negative charge from the active air according as the air was blown more or less gently through the cylinder.

It is to be noted that the charges received are not always of the same intensity, and to obtain them energetically it is necessary to insulate the tubes perfectly with paraffin, and also always with a glass stem.

The phenomena indicated above cannot be attributed to chemical actions, but on the contrary seem to be produced by a special rubbing of the active air upon metallic surfaces, as the result of which these assume one of the charges, while the other charge ought to manifest itself in the air. But from my very numerous measurements made upon the discharge of the electrometer produced by active air which has streamed against metallic cartouches connected to the soil, it results: (1) that the air had not lost all its discharging virtue, and (2) that it had a little of the charge of the cartouches (instead of having a charge of contrary sign to them) which it transported or conducted from them to the electrometer.

I have shown in another place* that active air by streaming against an electrified body is reduced either to ordinary air or to air charged with the electricity which disappears. Hence it may be supposed that the active air in rubbing upon the metallic surfaces develops the two electricities, one of which manifests itself upon these surfaces, and the other goes to reduce the active air to ordinary air, and therefore does not become manifest. Thus it might be explained also how active air streaming against these metallic surfaces is transformed into ordinary air. Therefore this is simply a hypothesis relative to phenomena which require further study.

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* Dell' azione dell' elettricità sulla virtù scaricatrice dell' aria ixata.—*Rendiconti dell' Accademia di Bologna*, 1899–1900.

Discussion.

The Chairman said he had observed the fact that metals were charged sometimes positively and sometimes negatively by active air.

Mr. Watson asked if any experiments had been performed on the viscosity of gases rendered active by X-rays.

C

L. *A Theory of Colloidal Solution.* *By* F. G. Donnan, *M.A., Ph.D., Junior Fellow, Royal University of Ireland* *.

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The main fact concerning "colloidal" solutions, a fact which has been established by experiment and thermodynamical reasoning, appears to be that such "solutions" are in reality complexes of *two* phases, of which one exists in a state of extremely fine division, interspersed throughout the other. It must be observed, however, that it is not a sufficient description to call such complexes mere "suspensions," for what we have here to deal with is not so much a certain sort of mixture or *pseudo-solution*, as rather a peculiar condition of matter, namely the "colloidal" state. This fundamental point was clearly emphasized by Graham, but seems to have been somewhat lost sight of by some modern writers. Thus Krafft † has proposed a theory of colloidal solutions in which it is supposed that the molecules of colloidally-dissolved substances rotate round each other in closed paths. Apart from the consideration that such a theory is invalid, inasmuch as it gives no explanation why these orbital systems should not possess translatory motion, it is evident that such a theory must, in any case, be highly unsatisfactory, for the really essential point would be the explanation of *how* such a state of affairs came about.

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* Read March 8, 1901.

† *Ber. d. d. Chem. Ges.* vol. xxix. p. 1334 (1896).

What we have to account for, in fact, is the following. A solid substance C, when brought in contact with certain liquid media, breaks up or disintegrates into these media, but in such a manner that the disintegration process *does not proceed to the molecular limit.* The liquid medium appears then to be interspersed with minute aggregates of C, which are still so much larger than molecular magnitudes that they are subjected to a statistically almost uniform molecular bombardment, and hence possess only very small quasi-molecular motions. These complexes, moreover, are such that changes of temperature, or the addition of comparatively small quantities of other substances, frequently cause the sudden precipitation in mass of the substance C.

In what follows an attempt is made to show that all these phenomena can be explained by the application of a well-known hypothesis, namely by means of Laplace's theory of intermolecular attractive forces. In doing this it is necessary, and in the present case essential, to carefully distinguish between the *kinetic molecular equilibrium* and the *statical** (mechanical) *equilibrium* at the interface of solid and liquid.

Let us consider first the state of affairs between a crystalline solid and a liquid medium which dissolves it.

Here we have, at any given temperature, a definite concentration of the dissolved solid. This equilibrium is a *molecular-statistical* one, and consists in the balancing of two statistically equal and oppositely directed molecular fluxes. At the same time, owing to the fact that a *definite interface* exists between the solid and the liquid, it is clear that any small volume-element of the solid lying near the interface is in *statical* equilibrium. The resultant of all the intermolecular forces is, in fact, an inwardly-directed force urging this volume-element towards the inner part of the solid.

Thus a crystalline solid immersed in its saturated solution is

(*a*) in statical equilibrium under a compressive stress ;
(*b*) in kinetic-molecular equilibrium under equal and opposite molecular fluxes.

Hence, during the process of solution of a crystalline solid, although there is a net outward flux of molecules, we must suppose that the resultant mechanical force acting on any small volume-element of the solid in the immediate neighbourhood of the solid–liquid interface remains inwardly directed, so that the "molar" integrity of the mass is preserved, although "molecular" disintegration is taking place.

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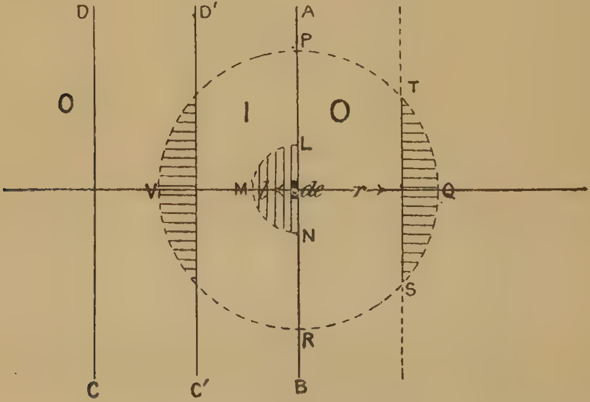
* In this connexion see Larmor, 'Æther and Matter' (1900), *passim.*

The theory which is here proposed for the pseudo-solution of colloidal matter regards this phenomenon as a process of *molar* or *mechanical* disintegration due to the non-existence of statical equilibrium in the thin surface-layers of the solid when the latter is in contact with certain liquid media.

Consider the solid, I, bounded by the planes AB, CD, and surrounded by the liquid medium O (it is sufficient to consider the problem in two dimensions). Let *de* be any small volume-element of I situated just at the bounding interface AB. Then *de* is acted on by two forces r and l, as indicated in the diagram, l being due to the attraction of I and r to that of O. For crystalline solids $l > r$; for "colloidal" matter in contact with certain liquids we *assume* that $r > l$.

Fig. 1.



It follows then that the solid I will begin to disintegrate into the liquid medium O. It is difficult to form an accurate mental picture of what exactly happens in this case. Probably the solid "mixes" into O in the form of excessively thin sheets or extremely fine and branching filaments. It must be observed that the colloidal solid is not in an "explosive" state, for the disintegration only affects at any moment the excessively thin surface-layers. The question now arises as to how far this process will continue; for if it be supposed to go on until the limit of molecular intermixture be arrived at, it is evident that a true solution must result. But as we understand by colloidal matter that condition of matter which gives "colloidal solutions" (defined by certain peculiar properties), it is clear that there exists something which arrests the disintegration-process before the molecular limit is arrived at, and yet at a point where the resulting "grain" is exceedingly fine. The essence of the theory here proposed lies in the nature of the assumptions whereby this stoppage of the process of disintegration or intermixture is accounted for.

Let the attraction of the matter contained in the semicircle PQR be a very large percentage of the attraction due to the infinite (or practically infinite) mass of O lying to the right of *de*. Let similarly the attraction due to LMN be the same very large percentage of the total attractive force exerted on *de* by the practically infinite mass of I. These circles correspond in fact to the so-called "spheres of molecular action." We *assume* that not only is $r > l$, but that also semicircle PQR > semicircle LMN.

The physical significance of these assumptions may be stated as follows:—It is assumed that the molecular "*adhesion*" between I and O is greater than the molecular "*cohesion*" of the colloid I, and that the intermolecular attractive forces fall off more rapidly with increasing distance in the case of the molecular cohesion of I than in the case of the adhesion between I and O. It is easy to express these conditions in a precise mathematical form by choosing a suitable law of force with two constants, but considering our present want of knowledge such a formulation could only serve the purposes of illustration.

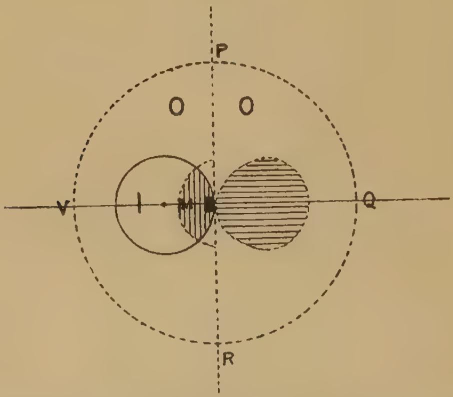
With the assumptions made, it now becomes possible to explain why the process of intermixture is arrested before the molecular limit. Suppose that the sheets, filaments, or particles have become so thin that the plane CD occupies a position C′D′ *within* the semicircle PVR (see fig. 1). Then it is evident that the value of r will be diminished since there now exists an effective component due to O acting on the *left* of *de*. In fact, the resultant attraction due to O bears a ratio to its former value equal to the ratio of PRST to semicircle PQR. At the same time, so long as the plane C′D′ lies within the semicircle PVR but *outside* LMN the value of the force l will not be sensibly altered.

Accordingly there exists a *critical* thickness of I such that the forces l and r just balance. When this state of division is reached the process of disintegration ceases, and there results a *two-phase* medium consisting of the medium I distributed throughout the medium O in some state of extremely fine division. Such a medium corresponds on the present theory to a colloidal solution.

Fig. 2, which requires no further explanation, applies to the case of *spherical* particles of I immersed in O.

If the medium O be continuously removed by evaporation or otherwise, or if sufficient of I be colloidally dissolved, there results an interlacing network of I distributed through O, and a more or less *elastic jelly* is produced (*cf*. the views of van Bemmelen).

Fig. 2.



For thicknesses of I greater than the critical, the medium I has a tendency to *increase* its common surface with O, *i.e.*, it possesses an effectively *negative* surface-tension. For thicknesses less than the critical, however, there will be a *positive* surface-tension. Hence if the substance I be produced in the medium O by chemical means, its aggregates will grow to this critical size and stop there, *i.e.*, will remain in colloidal solution.

If a colloid be defined as a substance which forms those pseudo-solutions termed colloidal, it follows from the above that this description is not sufficient unless the other medium, *i.e.* the *pseudo-solvent*, be specified. This point is well illustrated by the result obtained by Krafft * with the soaps; these substances give true solutions with alcohol, and colloidal solutions with water.

There is nothing to prevent a substance being partly colloidally distributed throughout a given medium and partly in true molecular solution †. Hence all gradations may occur. The foregoing considerations render intelligible many of the peculiarities exhibited by colloidal solutions, namely, their small diffusibility and small osmotic pressure, their frequent want of optical transparency, their "solidification" to jellies, their precipitation by changes of temperature or by the addition of comparatively small quantities of certain substances, &c., &c. It is necessary, however, to remark that only *reversible* changes admit of explanation on the above theory. The *irreversible* phenomena so frequently exhibited by organic colloids can only be explained by intra-molecular changes. As regards the nature of the "colloidal" state, as distinct from a colloidal solution, the present theory lends support to the view that in matter in the colloidal state the intermolecular forces are in general smaller than in the case of crystalline matter, and fall off comparatively rapidly with increasing distance. This view is in harmony with the fact that substances which tend to assume the colloidal condition are in general those which possess feeble powers of crystallization. A solid colloid is in fact an amorphous body possessing only an exceedingly minute velocity of crystallization. Whether, however, a colloid body is quite analogous to a highly supercooled viscous liquid with excessively small velocity of crystallization, such as "solid" glass, is not a question which I shall attempt to consider here. Some colour, is, however, given to this view by the recent work of Barus, who considers he has obtained colloidal solutions of glass in water.

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* *Ber d. d. chem. Ges.* xxvii. p. 1747; xxviii. p. 2556; xxix. p. 1328.

† So far as I am aware, this possibility was first mentioned by Mr. W. B. Hardy.

The whole question is intimately connected with the hitherto unsolved problem as to the real nature of the solid state.

Chemical Laboratory,
University College, London, W.,
Christmas, 1900.

Discussion.

Dr. Gladstone said that the study of colloids was one which had been too much neglected. It involves both a knowledge of physics and of chemistry. A colloid is an unstable body, and is always altering its composition. Water of combination may be given off at the ordinary temperature, even if the surrounding atmosphere is saturated, and the colloid cannot take up the water again. It is impossible to make a sharp distinction between colloids and crystalloids—they merge into one another. Transition forms are not uncommon.

Dr. Lehfeldt asked if it had been proved that colloids have osmotic pressure.

Prof. Threlfall said that in colloidal solutions some of the substance was not in suspension. Dr. Martin had filled a filter with silicic acid under pressure, and found that it allowed sugar solution to pass through, but stopped colloidal solutions. The author had used opacity as a test for colloids, but silicic acid could be got transparent. There are two kinds of opalescence. One cannot be removed, and exists because the substance is a two-phase system. The other can be removed with difficulty by filtering, and leaves a transparent substance. The want of transparency should be used cautiously as an argument.

Dr. Donnan, in reply to Dr. Gladstone's remarks on the transition from crystalloids to colloids, said that a substance might be a crystalloid with one medium and a colloid with another. In reply to Dr. Lehfeldt, he said that the only indisputable evidence in favour of osmotic pressure of colloids is that colloidal solutions diffuse. He agreed with Prof. Threlfall that opacity should be used carefully as an argument, but stated that his theory referred to a two-phase system.

LI. *A Direct-reading Conductivity-Bridge.*

By ROLLO APPLEYARD*.

30

WHEN it is required to check the conductivity of several tons of copper wire, of the same nominal diameter, the method employed generally resolves itself into making a careful test of the conductivity of the wire of a selected hank, and afterwards balancing a length of this on a slide-bridge against successive equal lengths of the remaining hanks of wire of that diameter. If an ordinary slide-bridge is employed, the scale-readings corresponding to the balance-position of the sliding contact are not directly proportional to the successive conductivities. To arrive at the conductivity a certain amount of arithmetic is necessary. If, however, the slide-bridge is arranged somewhat differently, the readings of the slider can be made to be directly proportional to conductivities.

Let a be the resistance of the selected wire of known conductivity k_a, and let b be the resistance of any of the remaining wires whose conductivity k_b is to be determined. The third arm of the bridge is a fixed resistance d, and the fourth arm is the slide-wire c, the resistance of which can be adjusted to balance d by moving the slider.

We have therefore,

$$\frac{d}{b}=\frac{c}{a}.$$

Or, replacing the reciprocals of b and a by their conductivities

$$dk_b=ck_a,$$

$$k_b=\frac{k_a}{d}c.$$

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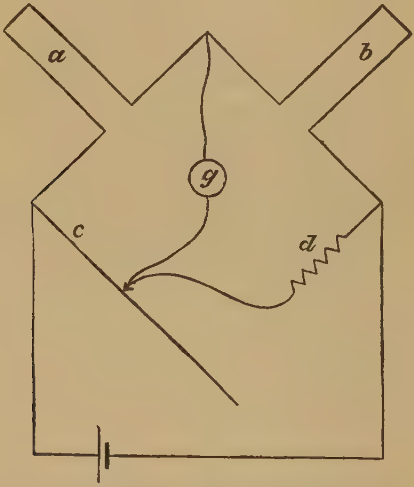
* Read March 8, 1901.

Hence the required conductivity k_b is given in terms of the slide-wire reading, multiplied by a constant k_a/d.

It is necessary that the contact between c and d should be invariable. The writer finds that the best contact is attained by a device resembling a drill-bow: the slider carries a small brass bow strung with one or more platinum wires, each of which passes once round the slide-wire. Vertical stops fixed to the slider prevent the platinum wires from lagging behind the bow as it is moved to right or left.



To graduate the slide-wire scale so that it shall read directly in conductivities, two values of b must be determined by any of the ordinary methods; these wires can then be put into position successively in the conductivity-bridge, and their balance positions marked on the scale. The whole length of the scale can then be divided in corresponding proportion, in equal divisions. The length of the equal divisions into which the scale is divided depends upon the diameter of the wire under test. It is convenient to be able to vary the length of these equal divisions, and also to be able to move the zero to right or left along the slide-wire. This can best be done by a parallel-ruler arrangement, the straight edges being in a vertical plane through the slide-wire. If the top straight-edge is then divided into equal parts, plumb-lines from those divisions divide the slide-wire into equal parts of any required length; and the parallel-ruler can be moved, as a whole, along the wire. The angle at which the straight-edge is set depends upon the diameter of the wire under test, the length being constant; the apparatus may therefore be calibrated in diameters as well as in conductivities.

LII. *On the Production of a Bright-Line Spectrum by Anomalous Dispersion and its Application the "Flash-Spectrum."* *By* Prof. R. W. Wood[*].

In a communication published in the Proceedings of the Royal Academy of Sciences, Amsterdam, W. H. Julius makes the very brilliant suggestion that the "flash-spectrum," seen immediately at totality, may be due to photosphere-light abnormally refracted in the atmosphere of metallic vapours surrounding the sun: in other words, the light of the flash-spectrum does not come from the reversing layer at all, but from the photosphere. The author shows that the light which will be thus abnormally refracted will be of wave-lengths almost identical with the wave-lengths which the metallic vapours are themselves capable of radiating. This beautiful theory not only explains the apparent shallowness of the reversing layer, a thing that has always puzzled astrophysicists, but it accounts for the extraordinary brilliancy of the lines.

I have succeeded in producing such a flash-spectrum by an arrangement in which I have endeavoured to imitate as closely as possible the conditions supposed to exist at the surface of the sun: in brief, I have obtained a spectrum of bright lines, with light from a source showing a continuous spectrum, by means of anomalous dispersion in an incandescent metallic vapour.

The theory of Julius supposes the sun to be surrounded by an atmosphere of metallic vapours, the refractive index of which decreases with increasing distance from the surface.

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[*] Read April 26, 1901.

In this atmosphere the rays of light coming from the photosphere will move in curved paths similar to rays in our own atmosphere.

The refractive index is, however, very small except for wave-lengths very near those which are absorbed by the vapour; consequently the light most strongly refracted, if it could be sorted out and examined with the spectroscope, would resemble very closely the light emitted by the vapours. Julius shows how this sorting out of the more refrangible rays may account for the bright-line spectrum usually attributed to the reversing layer, these rays moving in curved paths in the solar atmosphere, thus reaching us after the photosphere has been hidden by the moon.

For the reproduction of this phenomenon in the laboratory it is necessary to form an atmosphere of metallic vapour in which the refractive index changes rapidly from layer to layer. This I succeeded in accomplishing by allowing the flame of a Bunsen-burner, fed with metallic sodium, to play against the under side of a white plaster plate. On looking along the surface of the plate, it was seen that a dark space existed between the flame and the cold surface, resembling somewhat the dark space surrounding the cathode of a Crookes's tube. It seemed highly probable that, inasmuch as the temperature of the flame was lowered to such a degree by contact with the plate, the density of the sodium vapour would increase very rapidly from the surface of the plate downwards. The change may of course be abrupt instead of progressive, though I am inclined to favour the latter supposition. In either case the action will be practically the same, the case being similar to the transition from a curved ray to a broken-line ray, as the change of the index of the medium becomes less gradual. Having covered the under surface of the plaster plate with a non-homogeneous layer of sodium vapour, a spot at the edge of the flame was illuminated with sunlight concentrated by a large mirror. This spot radiated white light in every direction and corresponded to the incandescent photosphere of the sun. A telescope, provided with an objective direct-vision prism, was directed towards the white spot and moved into such a position that, owing to the reduction in the width of the source of light by foreshortening, the Fraunhofer lines appeared in the spectrum (fig. 1). This represents the stage of an eclipse when only the thin crescent of the sun is visible. The sodium-flame appeared superposed on the spectrum of course. On moving the spectroscope until it was well inside of the plane of the illuminated surface and feeding the flame with fresh sodium, the solar spectrum vanished, and there suddenly blazed out two narrow bright yellow lines almost exactly in the place of the sodium lines. Fig. 2 shows the inverted sodium-flame, the faint continuous spectrum and the "flash." Cutting off the sunlight with a screen caused the instant disappearance of the bright lines.

Fig. 1.

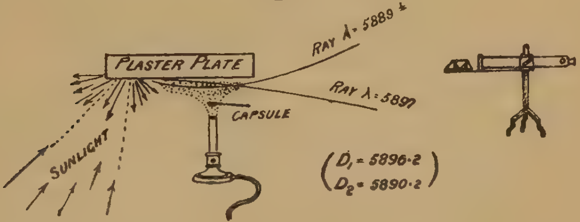
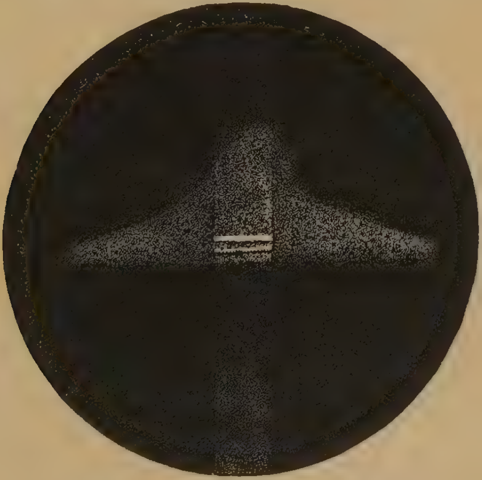


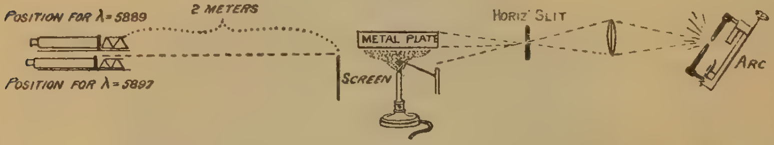
Fig. 2.—Flash Spectrum of Sodium produced by Anomalous Dispersion.



Repeating the experiment, I found that the bright lines came into view on the sides of the sodium lines towards the blue; that is to say, it is light for which the medium has an abnormally low refractive index that is bent around the edge of the plate and enters the instrument. This is precisely what we should expect, for sodium vapour has a refractive index of less than 1 for waves slightly shorter than D_1 and D_2, as was shown by Julius in his paper*. The rays then will be concave upward in a medium in which the refractive index varies, as I have supposed it to vary in the present case. If the sodium vapour is very dense, we see only a single bright line bordering D_2, owing to the complete absorption of the light between the lines.

I next instituted a search for the light of a wave-length slightly greater than that of the sodium lines. For these waves the vapour has a refractive index greater than 1, consequently the rays will be concave downward in the layer of vapour. (The paths are indicated on an exaggerated scale in fig. 1.) If we move our prismatic telescope down in a search for these rays, the solar spectrum will appear and drown out everything, but if we set up a screen (shown in fig. 3) in such a position as just to cut off the light from the illuminated spot, and feed the flame with sodium, we shall presently see bright lines appear on the side of the sodium lines towards the red. In this case, when the vapour is dense we get only a single line bordering D_1.

Fig. 3.



The arrangement described is inconvenient in many ways to work with, and I accordingly modified it in the following way:—

The light of an arc-lamp (fig. 3) is focussed on a horizontal slit, and a flat metal plate supported so that the plane in which its under surface lies coincides with the plane of the slit. The plate should be an inch or so thick, with a fairly level surface. At a distance of about two metres a telescope provided with a prism (direct-vision if possible), arranged so as to give a vertical spectrum, is placed at such a height that the prism barely catches the rays coming from the slit and grazing the surface of the plate. On looking into the telescope we see a bright continuous spectrum, and the telescope is to be raised until this becomes quite faint. The Bunsen-burner beneath the plate is now lighted, and a bit of sodium in a small iron capsule introduced into the centre of the flame. The results obtained are practically identical with those which have been described. I am now arranging apparatus by which I hope to obtain similar flash-spectra by the dispersion of vapours exhibiting more complicated absorption spectra than sodium. If these experiments are successful, much can be learned by comparing the flash-spectra with the emission-spectra. If it be found that certain lines are absent in the flash which are present in the emission-spectra, interesting comparisons can be made with photographs of the actual flash-spectrum of the sun. I am also engaged in making accurate determinations of the dispersion of metallic vapours by means of a metal prism of 45 degrees, furnished with mica windows. The prism is filled with hydrogen, and the metal—say sodium—vaporized in this atmosphere by the application of heat. The results obtained in this way are far superior to those yielded by prismatic flames. The angle of the prism is accurately known, and it is filled with non-luminous sodium vapour of uniform density and under known conditions of temperature and pressure. With this I have obtained much greater curvature of the spectrum in the vicinity of the absorption-lines than that figured by Julius (the total lateral bending in one case being 400 times the distance between the D lines), and the spectrum is perfectly steady instead of fluttering, as is the case when the deviation is effected by means of a sodium-flame of prismatic form. The work along these lines will be reported in a subsequent paper.

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* I have since found that the refractive index is less than 1 for the entire yellow, green, and blue portion of the spectrum, and greater than 1 for the entire red, orange, yellow end. In other words, I have obtained a complete anomalous spectrum with sodium vapour.

University of Wisconsin.

DISCUSSION.

Prof. HERSCHELL expressed his interest in the experiments, and their application to the case of the flash-spectrum seen at totality.

LIII. *The Thermal Properties of Isopentane compared with those of Normal Pentane.*

By J. ROSE-INNES, *M.A., B.Sc.*, *and* SYDNEY YOUNG, *D.Sc., F.R.S.*[*]

19

[Plate V.]

IN a paper read before the Physical Society in December 1898, attention was drawn to the great interest attaching to the comparison of the isothermals of two isomeric substances (Proc. Phys. Soc. xvi. p. 335; Phil. Mag. xlvii. p. 366). An experimental investigation of the relations between the temperatures, pressures, and volumes of isopentane had been carried out by one of us some time previously; and in the paper above referred to the results of a similar investigation into the thermal properties of normal pentane were given. A preliminary comparison was instituted between the thermal data belonging to the two substances respectively, and the conclusions provisionally arrived at were stated (*ll. cc.* pp. 335–6; pp. 366–7). We have since undertaken a more exhaustive examination of the experimental results, and the conclusions now reached form the subject of our present paper.

If we could treat normal pentane and isopentane as perfect gases, we should be able to write $pv = \mathrm{RT}$, where all the letters have their usual signification. In practice it is found that pv changes as p diminishes along any isothermal, in such a way that the limiting value of pv for $p=0$ is equal to RT; but any actual value of pv lies below RT within the limits of temperature of the experiments. The quantity $\mathrm{RT}-pv$, which should be zero if Boyle's law were correct, may be considered as measuring the error of Boyle's law, and we may term it "the departure from Boyle's law" for the particular volume and temperature in question. It then appears that the departure from Boyle's law in the case of isopentane bears a constant ratio to the departure for normal pentane at the same volume and temperature*. This simple law is found to yield numerical results so nearly in accordance with the experimental facts that the error incurred by assuming the law as entirely correct is comparable with the errors of experiment.

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[*] Read May 10, 1901.

We will next proceed to describe our method of testing the law. Take any volume and temperature, v and T say; and let p_n and p_ι denote the pressures of normal pentane and of isopentane respectively at the said volume and temperature. Then the departure from Boyle's law for normal pentane is $\mathrm{RT}-p_n v$, while the departure from Boyle's law for isopentane is $\mathrm{RT}-p_\iota v$. The proposed law tells us that

$$\frac{\mathrm{RT}-p_\iota v}{\mathrm{RT}-p_n v} = \text{a constant}$$

$$= \lambda, \text{ say.}$$

Hence we easily obtain

$$p_\iota v = \lambda p_n v + (1-\lambda)\mathrm{RT}.$$

By examining the experimental data in the neighbourhood of the critical point of normal pentane, it was concluded that λ might conveniently be put equal to ·9463. By the last formula it was then possible to calculate $p_\iota v$ for any volume and temperature whenever $p_n v$ for the same volume and temperature was known. In this way a large number of values of $p_\iota v$ were found for the isothermals 280° C., 240° C., 200° C., 160° C., 120° C. These were plotted in a diagram against $v^{-\frac{1}{3}}$, and the dots so drawn distinguished by means of a cross. The values of $p_\iota v$ found by direct experiment for the same temperatures were also plotted against $v^{-\frac{1}{3}}$, and the resulting dots distinguished by means of a small circle. As both sets of dots were very numerous, and occurred at small intervals of $v^{-\frac{1}{3}}$, we were well able to judge by the eye whether the curve determined by the one set might be considered as coinciding with the curve determined by the second set. The diagram is reproduced on Plate V. Only the volumes above 3·4 were taken into consideration, for reasons stated in our former paper (*ll. cc.* p. 333 ; p. 364).

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* The connexion between chemical problems and the departure from Boyle's law has also been investigated by M. Daniel Berthelot. (See *Comptes Rendus*, 1898, cxxvi. pp. 954, 1030, & 1415.) His immediate object, however, was different from ours. He confined himself to studying how the departures from Boyle's law might be allowed for in deducing the true molecular weights of substances by physical methods; and he nowhere pays special attention to isomeric bodies.

It will be seen that on the whole the two sets of dots agree very well. In places, however, there is a discrepancy between the two sets: *e. g.*, at small volumes on the isothermal of 240° C. the calculated values of pv differ from the experimental values by slightly over 1 per cent. This error is partly to be accounted for by our not having chosen the most suitable value of λ; by choosing a rather smaller value we could easily diminish the error spoken of. But we cannot diminish the error indefinitely in this way, since we are hampered by the condition that we must not introduce more serious error into fresh places by our changes in λ. Hence there will necessarily be some small outstanding differences between the two sets of dots whatever value of λ be chosen. We have not thought it worth while to draw a fresh diagram with a more suitable value of λ, as a slight correction in the diagram corresponding to a slight change in λ is easily allowed for by the eye.

As to whether the outstanding differences referred to above indicate the necessity for a correction in the law we have proposed, or whether they can be considered as due to errors of experiment, we are unable to decide with any confidence at present. But it seems certain that by far the greatest part of the difference in the behaviour of normal pentane and of isopentane can be attributed to the action of the law we have mentioned. We are therefore confirmed in the conclusion stated by us in a former paper "that the difference of pressure between two isomeric substances at the same temperature and volume involves the same power of the density as the first deviation from Boyle's law, *i. e.* the second power" (Phil. Mag. xlviii. p. 214).

DISCUSSION.

Mr. MACFARLANE GRAY said the numbers obtained would be valuable to himself, and to all those who theorized on other people's experiments. He was sorry, however, that the authors had dealt with empirical formulæ instead of rational formulæ deducible from the theory of gases.

Dr. Chree asked how the temperatures were measured.

Mr. Rose-Innes said recourse had been had to empirical formulæ because they found theoretical formulæ useless. He gave examples of the failure of well-known equations to satisfy experimental results. The temperatures were measured with a constant-volume air-thermometer, a small correction — less than the errors of experiment — being employed to reduce the readings to the thermodynamic scale.

LIV. *The Magnetic Properties of the Alloys of Cast-Iron and Aluminium.*—Part II. *By* S. W. Richardson, *D.Sc., Principal and Professor of Physics at the Hartley College, Southampton, and* Louis Lownds, *B.Sc.*, 1851 *Exhibition Research Scholar, University College, Nottingham.*[*]

36

[Plate VI.]

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§ I. *Introduction.*

An account of a series of experiments performed by one of us on the magnetic properties of certain impure alloys of iron and aluminium is given in the Philosophical Magazine for January 1900[†]. As the results obtained from these experiments were of a very interesting character, the authors thought it desirable to undertake further experiments on the magnetic behaviour of these specimens.

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[*] Read June 8, 1900.

[†] Proc. Phys. Soc. vol. xvii. pp. 1–38.

Experiments were accordingly made in the first instance to ascertain in what way the hysteresis-loss, between given limits of the field-strength, was connected with the temperature for the specimen containing 3·64 per cent. of aluminium.

As will be seen later, these experiments show that the hysteresis-loss attains a maximum value at a temperature considerably higher than the temperature of maximum induction.

An account is also given of some experiments on the changes produced in the magnetic properties of the alloy by heating to a high temperature and subsequently cooling. It is shown that the magnetic properties depend largely on the previous history of the specimen; successive curves connecting the maximum induction obtained for any given value of the field-strength and the temperature differing from one another to some extent when the heating has been carried to a high temperature. This difference has been found to be greater for weak than for strong fields.

There does not, however, appear to be any essential difference between the behaviour of this alloy during heating and cooling (except near the *temperature of minimum permeability*, *e. g.* critical temperature).

Similar results have been obtained for the specimen containing 5·44 per cent. of aluminium. For the specimen containing 9·89 per cent. of aluminium, however, no change in the magnetic properties could be detected due to heating and cooling unless the heating was continued to about 670° C., which temperature is about 220° higher than the temperature of minimum permeability for this specimen (*e.g.* 450° C.). In addition an account is given of some experiments on the abrupt change in the permeability that takes place at a temperature of 652° C. (*vide* p. 139, Phil. Mag. Jan. 1900).

The Ballistic method was used for determining the hysteresis-loss; and the Balance method (*vide* Part I.) for obtaining the smaller values of the induction when the specimen was near the temperature of *minimum permeability.*

The specimen in the form of a ring was wrapped round with asbestos-paper. Next to this was twisted the thermometer-wire which consisted of platinum wire of ·2 millim. diameter. This wire was connected to platinum leads of ·5 millim. diameter.

Compensating leads, cut from the same specimen of wire, passed out along with these between the primary and secondary winds.

The primary and secondary coils, which were of copper wire and insulated with asbestos-paper, came next, and externally a well-insulated platinum wire (diam. ·5 millim.) was wound non-inductively round the ring.

The specimen was heated electrically, this non-inductively wound platinum wire being used as a heating circuit. The specimen, with the surrounding coils, was packed in asbestos waste and placed in a sand-bath. Experiments were made at temperatures ranging from 15° C. to 800° C.

The conclusions arrived at from these experiments are as follows :—

(1) The hysteresis-loss at first diminishes as the temperature rises. It then increases and reaches a maximum value at about 550° C., which temperature is about 80° higher than the temperature of maximum induction. On further heating it falls off rapidly and becomes negligible at about 700° C.

(2) The magnetic properties of the specimen depend largely on its previous history.

(3) There is no essential difference between the behaviour of this specimen during heating and cooling* (except near the temperature of minimum permeability).

(4) An abrupt increase in the permeability takes place at 652° C. (during heating) followed by an equally abrupt diminution on further heating.

(5) This abrupt change in the permeability is more marked with falling than with rising temperatures.

(6) Continued heating and cooling diminish the permeability of this specimen (probably due to disintegration)*.

(7) The curve connecting the temperature of minimum

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* This statement does not hold for specimens containing only a small quantity of impurity, as will be shown in a subsequent communication.

permeability and the percentage of aluminium for the specimens investigated is a straight line.

(8) The microscopic examination of the specimens shows the presence of crystals.

§ II. *The Magnetic Measurements.*

The first series of experiments was made with a view to ascertaining in what way the hysteresis-loss between given limits of the field-strength was connected with the temperature of the specimen. The ballistic method of measuring the induction was made use of in this set of experiments.

The experimental arrangement was roughly as follows:—

The secondary of the ring was joined up in series with the secondary of a standard mutual inductance-coil and a D'Arsonval ballistic galvanometer.

A known standardizing current was then sent through the primary of the mutual inductance-coil and the throw of a spot of light (reflected from the mirror of the galvanometer on to a transparent scale) on reversing the current was noted.

Then if

M = the value in C.G.S. units of the standard mutual inductance;
γ = the value of the standardizing current;
d = the throw of the spot of light;
k = some constant;

we have

$$M\gamma = kd$$

or

$$k = \frac{M\gamma}{d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The primary of the standard mutual inductance-coil was then disconnected, and a current was sent through the primary of the ring and an adjustable resistance. This current was then varied 'by steps,' and the throw corresponding to any change $\delta\gamma$ in the current strength was noted.

Then if

N = the number of turns in the secondary of the ring;
S = the mean sectional area of the ring;
δB = the change in the induction in the ring corresponding to a change $\delta\gamma$ in the current strength;
d' = the throw of the spot of light;

we have

$$\delta B . S . N = kd'$$

or

$$\delta B = k \frac{d'}{SN} . \qquad (2)$$

Combining (1) and (2) we obtain the equation

$$\delta B = \frac{M . \gamma}{d} . \frac{d'}{S . N} .$$

The Primary Circuit.

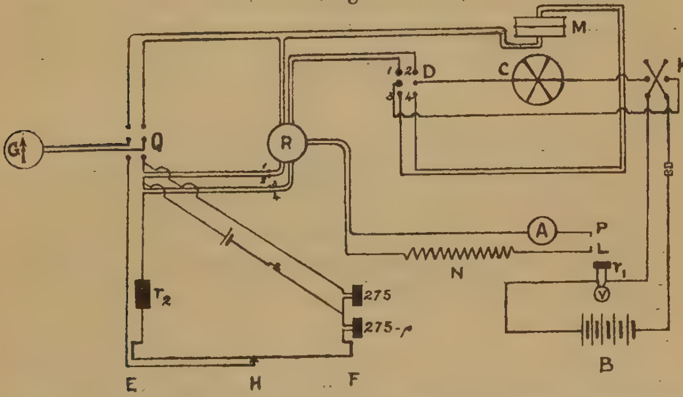
The ring was wound with a primary coil of 42 turns of copper wire insulated with asbestos-paper.

The primary was connected to the two mercury cups 1 & 2 of the rocker D (*vide* fig. 1).

To the cups 3 & 4 of this rocker were connected the terminals of the primary of the mutual inductance-coil M.

This rocker enabled the battery B to be connected at will to either the primary of the ring R or the primary of the standard mutual inductance-coil M.

Fig. 1.



The rocker D was directly connected to a variable resistance C and a reversing-key K.

To K was connected a battery of five storage-cells B and a Weston's voltmeter V, to the terminals of which was attached a resistance r_1.

The value of this resistance was one ohm, and hence the reading of the voltmeter in volts was numerically equal to the primary current in amperes.

This resistance was composed of thick platinoid wire twisted spirally and suspended by threads in a box with perforated sides and cover to allow the free circulation of air round the wire.

It was found by trial that the resistance of this coil was not appreciably changed by the passage of the greatest current used in the experiments.

The adjustable resistance C consisted of a number of coils of platinoid wire attached to a brass frame. The free ends of these coils were connected to a series of stops on the upper circle. Contact was made by means of a T-shaped brass arm revolving round the axis of the frame, and of such dimensions as to enable the resistance to be varied without breaking the circuit. This arrangement of coils was found very convenient for varying the current 'by steps.'

The Secondary Circuit.

The secondary of the ring and the secondary of the mutual inductance-coil were connected permanently to one another throughout the experiments. This circuit could be connected when desired to the galvanometer terminals by means of the rocker Q.

The galvanometer was a Crompton Midget D'Arsonval, and was suitable for ballistic or deflective zero work.

This instrument consists of a circular coil suspended bifilarly between the poles of a permanent magnet. The suspending fibres, which are of bronze, serve to carry the current. The galvanometer was very dead-beat and consequently the throws could be read with considerable ease.

The secondary circuit was kept closed throughout a series of readings, and the throws were always taken in the same direction. The kind of accuracy obtainable with this instrument can be seen from the following observations. The primary of the standard mutual inductance-coil was connected to the battery, and three successive readings of the kick obtained on reversing the current in the primary were taken for currents of different strengths, The following set of readings were obtained :—

Current in Amperes.	Throws.				Throw ÷ current.
	1.	2.	3.	Mean.	
1·42	152	149	151	150·7	106·1
1·075	114·5	113	115	114·2	106·2
0·782	83	83	82·5	82·8	105·9
0·27	28·5	29	28·5	28·7	106·3

It will be seen from this table that the instrument is suitable for ballistic work.

The value of the standard mutual inductance-coil was 533,626 C.G.S. units. Its value was obtained by Mr. C. G. Lamb by comparison with a standard coil kept in the Engineering Laboratory at Cambridge.

§ III. *The Measurement of Temperature.*

The method used for measuring the resistance of the thermometer-wire was the same, in all essentials, as that described in Part I. (Phil. Mag. Jan. 1900 ; Proc. Phys. Soc. vol. xvii. pt. 1). The four arms of the bridge consisted of

(1) The thermometer-wire and leads.

(2) The compensating leads, a resistance r_2, and a portion of the bridge-wire EH.

(3) A resistance of 275 ohms.

(4) A resistance of $(275-\rho)$ ohms + portion of bridge-wire HF.

[ρ being equal to the resistance of H F to within $\frac{1}{20}$ of an ohm.]

When a balance is obtained, the resistance r_t of the thermometer-wire is given by

$$r_t = r_2 + \text{resistance of E H}.$$

The temperature was deduced from r by means of the formula

$$t = 100\frac{r_t - r_0}{r_{100} - r_0} + \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}.$$

The values of r_0, r_{100}, and δ for the given specimen of wire were determined from observations of its resistance in ice, steam, and the vapour of boiling sulphur.

This specimen of wire was obtained from Johnson & Matthey, and was of the quality prepared by this firm for thermometer work.

For this wire $\delta = 1{\cdot}57$

and $r_{100} = r_0(1 + 0{\cdot}377)$.

§ IV. *The Heating Circuit.*

The heating circuit consisted of a platinum wire, of diameter 0·5 mm., well insulated with asbestos-paper, and wound non-inductively round the ring outside the other coils. This wire was connected with an ammeter A (*vide* fig. 1), an adjustable resistance N of thick platinoid wire, and the terminals of the town mains (100 volts) P, L. By altering the value of the resistance N the heating current could be varied at will, and thus any required temperature (within the limits of the experiments) could be obtained.

With this arrangement a current of 7 amperes raised the temperature of the ring above 800° C.

The insulation resistance between the various coils was tested from time to time during the experiments. In no case (after the first heating) was it less than 1,000,000 ohms, and in general it probably was much greater than this.

§ V. *Connexion between Hysteresis Loss and Temperature.*

It had been observed in the earlier experiments that the curve connecting the maximum induction reached at each reversal and the temperature for a given value of the field-strength altered to some extent after the specimen had been heated to a high temperature. This was also found to be the case with the specimen containing 5·44 per cent. of aluminium.

In the case of the other two specimens investigated, however (the one containing 9·89 and the other 18·47 per cent. of aluminium), this was not the case, unless the temperature reached was much higher than the temperature of minimum permeability.

For the alloy containing 9·89 per cent. of aluminium the curve was quite constant under all conditions, unless the specimen was raised to a temperature of 670° C. (*i. e.* 220° above the temperature of minimum permeability), in which case a new curve of the same general shape as the original curve was obtained.

The change in this case may be due to the specimen reaching the melting-point of aluminium. That conclusion, however, is not borne out by the experiments on other specimens, as in general a noticeable change takes place at a temperature considerably lower than this.

In order to obtain comparable results, the loops were taken in the order of increasing temperature: the temperature on any day on which an experiment was made being higher than that reached in the preceding experiment.

The experiments were conducted under the following conditions:—

At about 10 A.M. the heating current necessary to produce the required temperature was started in the heating circuit.

A steady temperature was, in general, reached at about 3 P.M.

The specimen was kept at this temperature till about 5 P.M., to ensure a uniformity of temperature when a loop was taken.

The specimen was then allowed to cool, and the process of re-heating was commenced on the following day *.

In some cases several loops were taken in one day. When this was so, the higher temperatures were obtained without first cooling the specimen to the temperature of the room.

The standardising throw was taken before and after the observations for each hysteresis-loop.

The loops obtained are shown on Plate VI.

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* This method is spoken of as the method of *successive heatings.*

Data.

Temp. 24° C.		Temp. 159° C.		Temp. 226° C.		Temp. 311° C.	
H. c.g.s. units.	B. lines per sq. cm.	H. c.g.s. units.	B. lines per sq. cm.	H. c.g.s. units.	B. lines per sq. cm.	H. c.g.s. units.	B. lines per sq. cm.
8·20	3089	8·20	3108	8·20	3147	8·20	3309
6·64	2956	6·64	2956	6·64	2994	6·64	3156
4·81	2765	4·81	2727	4·81	2784	4·81	2927
3·36	2575	3·36	2517	3·36	2574	3·36	2736
2·18	2365	2·18	2327	2·18	2346	2·18	2526
1·06	2155	1·06	2098	1·06	2098	1·06	2260
·47	2021	·47	1964	·47	1983	·47	2107
0	1850	0	1793	0	1812	0	1936
− ·47	1754	− ·47	1659	− ·47	1678	− ·47	1764
−1·06	1487	−1·06	1392	−1·06	1374	−1·06	1402
−2·18	648	−2·18	362	−2·18	133	−2·18	− 372
−3·36	− 820	−3·36	−1125	−3·36	−1363	−3·36	−1783
−4·81	−1983	−4·81	−2117	−4·81	−2250	−4·81	−2507
−6·64	−2708	−6·64	−2746	−6·64	−2822	−6·64	−3022
−8·20	−3089	−8·20	−3108	−8·20	−3147	−8·20	−3309
July 21.		July 21.		July 24.		July 25.	

Temp. 361° C.		Temp. 370° C.		Temp. 381° C.		Temp. 392° C.	
H.	B.	H.	B.	H.	B.	H.	B.
8·20	3318	8·20	3318	8·20	3213	8·20	2890
6·64	3185	6·64	3185	6·64	3080	6·64	2772
4·81	2994	4·81	2975	4·81	2889	4·81	2595
3·36	2784	3·36	2765	3·36	2698	3·36	2418
2·18	2555	2·18	2498	2·18	2470	2·18	2241
1·06	2307	1·06	2288	1·06	2241	1·06	2005
·47	2155	·47	2136	·47	2088	·47	1868
0	1926	0	1983	0	1878	0	1691
− ·47	1812	− ·47	1793	− ·47	1745	− ·47	1514
−1·06	1392	−1·06	1373	−1·06	1306	−1·06	1081
−2·18	− 839	−2·18	− 972	−2·18	−1020	−2·18	− 983
−3·36	−2040	−3·36	−2136	−3·36	−2069	−3·36	−1868
−4·81	−2651	−4·81	−2689	−4·81	−2603	−4·81	−2339
−6·64	−3070	−6·64	−3070	−6·64	−2984	−6·64	−2693
−8·20	−3318	−8·20	−3318	−8·20	−3213	−8·20	−2890
July 26. Insulation tested. $R > 10^6$ ohms.		July 26.		July 26.		July 28.	

Data.

Temp. 416° C.		Temp. 449° C.		Temp. 460° C.		Temp. 502° C.	
H.	B.	H.	B.	H.	B.	H.	B.
8·20	2625	8·20	2487	8·20	2389	8·20	2239
6·64	2507	6·64	2393	6·64	2301	6·64	2151
4·81	2349	4·81	2257	4·81	2177	4·81	2027
3·36	2212	3·36	2124	3·36	2053	3·36	1903
2·18	2074	2·18	1991	2·18	1929	2·18	1797
1·06	1897	1·06	1832	1·06	1770	1·06	1673
·47	1779	·47	1726	·47	1681	·47	1602
0	1602	0	1584	0	1487	0	1478
− ·47	1524	− ·47	1460	− ·47	1451	− ·47	1407
−1·06	1150	1·06	1106	−1·06	1168	−1·06	1195
−2·18	− 875	−2·18	− 858	−2·18	− 584	−2·18	− 292
−3·36	−1701	−3·36	−1637	−3·36	−1487	−3·36	−1319
−4·81	−2133	−4·81	−2044	−4·81	−1912	−4·81	−1779
−6·64	−2448	−6·64	−2328	−6·64	−2212	−6·64	−2080
−8·20	−2625	−8·20	−2487	−8·20	−2389	−8·20	−2239
July 28.		Aug. 15. Insulation tested. $R > 10^6$ ohms.		Aug. 18.		Aug. 16. Insulation tested. $R > 10^6$ ohms.	

Temp. 569° C.		Temp. 582° C.		Temp. 602° C.		Temp. 642° C.	
H.	B.	H.	B.	H.	B.	H.	B.
8·20	1690	8·20	1354	8·20	637	8·20	221
6·64	1620	6·64	1301	6·70	584	6·64	203
4·81	1513	4·81	1212	4·93	513	4·81	168
3·36	1425	3·36	1124	3·45	460	3·36	142
2·18	1319	2·18	1053	2·30	389	2·18	124
1·06	1230	1·06	965	1·12	336	1·06	97
·47	1177	·47	912	·53	301	·47	80
0	1106	0	841	0	283	0	62
− ·47	1053	− ·47	788	− ·53	230	− ·47	44
−1·06	929	−1·06	664	−1·12	159	−1·06	9
−2·18	593	−2·18	398	−2·30	− 18	−2·18	− 62
−3·36	− 27	−3·36	80	−3·45	−159	−3·36	−115
−4·81	− 929	−4·81	− 558	−4·93	−336	−4·81	−150
−6·64	−1460	−6·64	−1124	−6·70	−513	−6·64	−186
−8·20	−1690	−8·20	−1354	−8·20	−637	−8·20	−221
Aug. 18. Insulation tested. $R > 10^6$ ohms.		Aug. 24.		Aug. 25.		Aug. 30. Insulation tested. $R > 10^6$ ohms.	

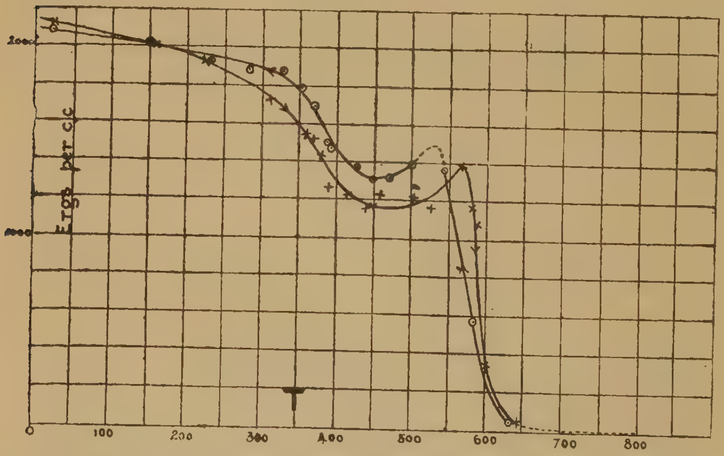
It has been stated that the B and T curves (H = a constant) change to some extent after the specimen has been raised to a high temperature. It was hence thought desirable to obtain a set of hysteresis-loops while the alloy cooled, to see whether there was any essential difference between its behaviour during the processes of heating and cooling.

Accordingly the specimen was heated to 800° C., and allowed to cool by stages down to the temperature of the room.

Double reversal throws and loops were taken at intervals when the temperature was steady.

This series of experiments lasted 26 hours, both the authors being present throughout the experiments.

Fig. 2.



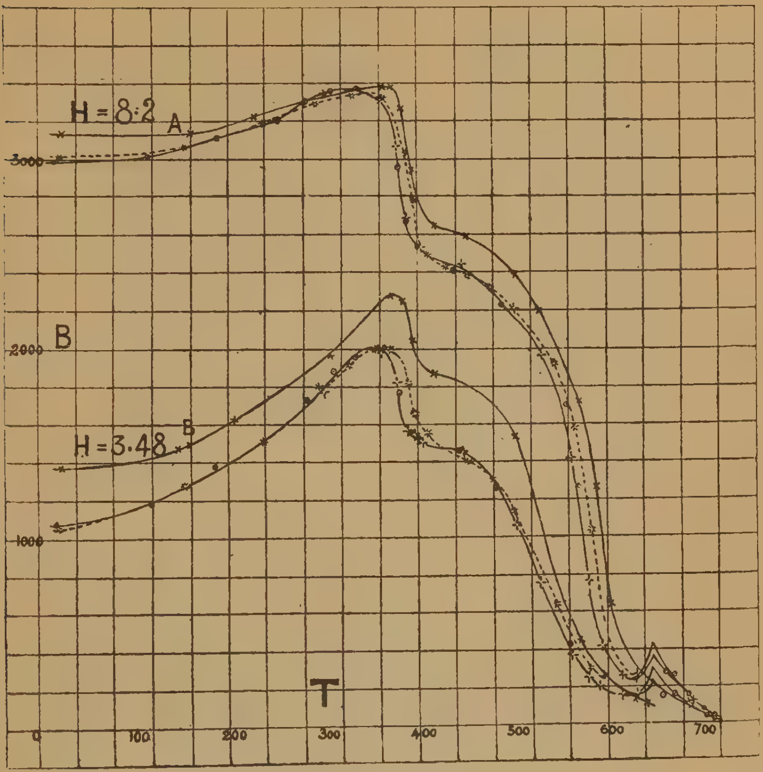
The curves of double reversals will be seen to be different from those obtained by successive heatings (*vide* fig. 3), though, as will be seen later, the curves obtained from consecutive heatings and coolings approximate much more nearly to one another.

As a check on the results, the ring was unwound and then re-wound with cotton-covered copper wire soaked in melted paraffin, and again tested. The values obtained in the two cases were found to confirm one another.

The loops obtained are shown on Plate VI.

The hysteresis loss was calculated in each case and curves connecting the hysteresis loss and the temperature for the given limits of field-strength are shown as fig. 2.

Fig. 3.



Data.

H.	583° C.	544° C.	501° C.	471° C.	454° C.	428° C.
	B.	B.	B.	B.	B.	B.
8·20	982	1757	2084	2204	2257	2336
6·90	912	1686	2013	2133	2186	2265
5·25	823	1615	1925	2027	2080	2159
3·84	735	1527	1828	1912	1956	2044
2·60	646	1403	1686	1788	1832	1885
1·33	540	1314	1580	1646	1681	1743
·59	487	1252	1492	1558	1584	1637
0	451	1102	1358	1425	1460	1469
−·59	345	1075	1261	1327	1345	1389
−1·33	204	872	1013	1080	1071	1089
−2·60	−62	243	−173	−434	−540	−593
−3·84	−239	−642	−1181	−1372	−1460	−1496
−5·25	−469	−1226	−1659	−1797	−1867	−1920
−6·90	−770	−1590	−1943	−2062	−2115	−2186
−8·20	−982	−1757	−2084	−2204	−2257	−2236

Data.

H.	394° C.	388° C.	370° C.	354° C.	330° C.	234° C.
	B.	B.	B.	B.	B.	B.
8·20	2690	2912	3151	3221	3195	3053
6·90	2602	2805	3045	3115	3089	2947
5·25	2460	2646	2886	2956	2929	2788
3·84	2301	2487	2727	2779	2752	2593
2·60	2142	2257	2515	2602	2558	2416
1·33	1929	2062	2320	2372	2328	2186
·59	1788	1938	2178	2213	2186	2044
0	1646	1798	1965	2018	2009	1850
− ·59	1434	1620	1805	1859	1832	1708
−1·33	1062	1230	1381	1451	1443	1389
−2·60	− 796	− 805	− 885	− 796	− 646	− 443
−3·84	−1752	−1920	−2106	−2071	−2009	−1584
−5·25	−2212	−2416	−2637	−2655	−2628	−2345
−6·90	−2496	−2735	−2974	−3027	−3000	−2805
−8·20	−2690	−2912	−3151	−3221	−3195	−3053

151° C.		151° C.		21° C.		21° C.	
H.	B.	H.	B.	H.	B.	H.	B.
8·20	2982	− ·59	1602	8·20	2951	− ·59	1582
6·90	2876	−1·33	1301	6·78	2840	−1·30	1304
5·25	2717	−2·60	168	5·13	2674	−2·54	379
3·84	2540	−3·84	−1319	3·78	2489	−3·78	−1008
2·60	2363	−5·25	−2186	2·54	2286	−5·13	−2026
1·33	2115	−6·90	−2700	1·30	2064	−6·78	−2636
·59	1956	−8·20	−2982	·59	1916	−8·20	−2951
0	1832			0	1804		

The observations obtained from the experiments with rising temperatures are indicated thus ×, and those obtained from the experiments with falling temperatures ⊙.

It will be seen that the curves develop maxima at the temperatures 570° and 530° C. respectively.

If these curves be compared with the corresponding double reversal curves fig. 3, it will be seen that the hysteresis loss falls off as the induction increases, reaches a minimum value at a temperature about 100° higher than the temperature of maximum induction, and attains a second maximum when the induction has about half its maximum value.

Variation of Hysteresis Loss with Temperature.
Limits of Field-strength +8·2 and −8·2.

Experiments with rising Temperatures.		Experiments with falling Temperatures.	
Temperature in degrees cent.	Hysteresis Loss in ergs per c.c.	Temperature in degrees cent.	Hysteresis Loss in ergs per c.c.
24	2132	21	2092
159	2019	151	2035
226	1939	234	1940
311	1733	284	1892
361	1550	330	1892
370	1526	354	1796
381	1447	370	1700
392	1272	388	1502
416	1240	394	1478
441	1161	428	1383
449	1177	454	1320
460	1240	471	1335
502	1224	501	1400
527	1178	544	1368
569	1399	583	588
582	1178		
587	1082		
602	354		
642	57		

The relation between the Coercive Force and the Temperature is shown on Plate VI., and was obtained from the following readings :—

With rising Temperatures.		With falling Temperatures.	
Temperature.	Coercive Force.	Temperature.	Coercive Force.
24° C.	2·7	21° C.	2·9
159	2·5	151	2·7
226	2·3	234	2·4
311	2·0	284	2·3
361	1·8	330	2·3
370	1·7	354	2·1
381	1·6	370	2·1
392	1·5	388	2·1
416	1·8	394	2·2
441	1·7	428	2·3
449	1·7	454	2·2
460	1·8	471	2·4
502	2·0	501	2·5
527	2·2	544	2·9
569	3·3	583	2·4
582	3·4		
587	3·6		
602	2·2		

§ VI. *Experiments on the Changes in the B and T curves due to successive Heatings and Coolings.*

The magnetic properties of the specimen change to some extent after heating to a high temperature.

The difference between two successive B and T curves (H=a constant) is much smaller for strong than for weak fields.

In all the cases tried the characteristic form of the curve was maintained. The nature of this change can be seen from a consideration of the curves shown on fig. 3.

The curves A and B were obtained from double reversal throws taken simultaneously with the hysteresis loops for rising temperatures.

They were plotted from readings which are indicated on the diagram thus ×.

In the figures T stands for the temperature in degrees centigrade, B for the maximum induction reached at each reversal, and H for the field-strength in C.G.S. units.

H=8·2 C.G.S. units.		H=3·48 C.G.S. units.	
T.	B.	T.	B.
24	3137	24	1364
159	3137	146	1468
226	3223	157	1487
311	3337	165	1535
361	3376	204	1621
370	3376	228	1697
381	3261	307	1955
392	2939	312	2021
416	2644	370	2269
449	2584	382	2241
502	2381	392	2035
527	2195	415	1858
569	1708	500	1522
582	1389	570	442
587	1257	594	248
602	628	640	106
642	221		

The specimen was then heated to 800° C., and double reversal throws were taken for fields of 8·2 and 3·48 units during cooling.

The values obtained are indicated thus * in fig. 3.

It will be seen that the magnetic properties have changed considerably owing to the repeated heatings and coolings.

H=8·2.		H=3·48.	
T.	B.	T.	B.
696	168	696	106
638	274	638	142
582	1027	580	292
564	1567	544	637
541	1910	500	1123
500	2195	477	1291
474	2319	450	1397
452	2380	428	1451
428	2425	408	1520
408	2495	394	1647
394	2780	388	1813
386	3035	369	1990
369	3265	360	1990
360	3320	354	1990
354	3320	326	1902
330	3328	293	1795
291	3293	235	1505
235	3185	152	1274
152	3062	20	1045
20	3015		

The specimen was next slowly heated to 434° C. and then slowly cooled, double-revesal throws being taken at intervals; the readings (not given) were found to lie on the last curve obtained.

The specimen was then unwound and rewound with cotton-covered copper wire soaked in melted paraffin, and double-reversal throws were taken at ordinary temperatures. The values obtained confirmed the preceding observations.

The ring was now wound with asbestos-insulated copper wire, the number of turns in the primary and secondary being the same as in the previous experiments with asbestos insulation.

The specimen was then heated by stages to 720° C. and cooled, double reversals being taken at each stage when the temperature was steady. This experiment lasted 36 hours.

These values are indicated on the diagram thus:—

⊙ for observations during heating,

⊹ for observations during cooling.

Observations during heating, indicated on fig. 3 thus, (·).

H=8·2.		H=3·48.	
T.	B.	T.	B.
16·5	2988	16·5	1064
114	3015	117	1175
186	3117	184	1369
251	3200	254	1516
280	3302	280	1720
307	3358	309	1877
334	3367	332	1942
360	3311	362	1998
377	2951	378	1757
387	2664	389	1583
398	2534	398	1517
436	2405	441	1452
487	2220	481	1249
555	1683	559	416
660	268	657	139
669	250	670	148
684	166	683	111
700	65	703	37
711	37	711	18

Observations during cooling indicated thus –|– on fig. 3.

H=8·2.		H=3·48.	
T.	B.	T.	B.
688	111	683	102
630	240	630	129
628	222	628	120
614	250	614	129
593	407	590	194
577	758	578	240
560	1406	560	361
528	1952	527	740
500	2201	502	1045
444	2442	444	1443
401	2534	402	1489
394	2553	394	1535
386	2682	387	1554
376	3062	376	1813
360	3311	360	1970
300	3340	298	1767
298	3367		

The curves obtained from these last two sets of readings approximate closely to one another throughout the greater part of their length. The authors have been led to the conclusion that the heating- and cooling-curves for this alloy are coincident only when the highest temperature reached in the experiments is considerably less than the temperature of minimum permeability. When the temperature approaches this value the magnetic properties of the specimen change, and a new curve connecting the induction and temperature is obtained.

Table of Values of H and B at Atmospheric Temperatures.

I. From Observations in 1897.		II. From Observations in March 1900.	
H.	B.	H.	B.
0·94	216	0·6	93
1·55	469	1·04	208
2·20	675	1·73	375
3·45	1674	2·88	853
4·40	2200	4·03	1435
5·39	2614	5·76	2187
6·59	2990	6·91	2540
7·82	3294	8·63	2980
8·99	3540	11·50	3480
9·40	3630	12·65	3620
11·19	3906	14·38	3835
13·19	4180	17·27	4125
14·87	4394	20·93	4415
18·36	4720	23·85	4620
27·20	5310	26·72	4785
32·70	5680	29·60	4975
33·00	5670	32·47	5145

In the accompanying table is given a series of values of the induction and field strength at ordinary temperatures, obtained (i.) in the summer of 1897, and (ii.) in March 1900.

The two curves connecting them are shown as I and II on fig. 4. It will be seen from these curves that the effect of repeated heating and cooling is to diminish the permeability of the specimen.

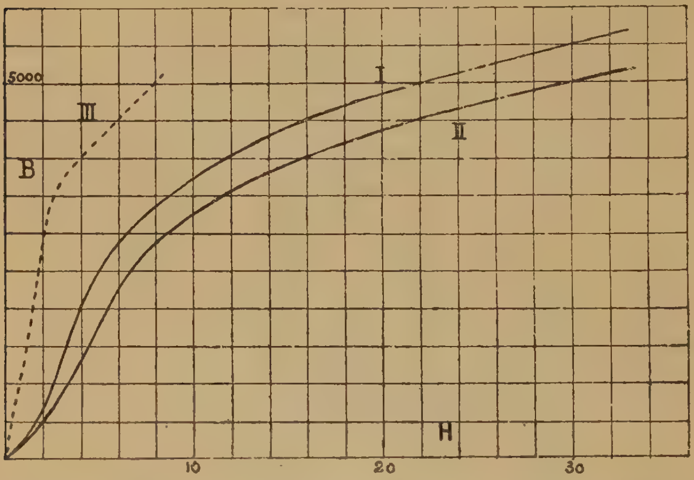
Let us seek for an explanation of this unexpected result.

It is known that impure specimens of iron containing large amounts of aluminium disintegrate in course of time. It is hence not unlikely that the same process is at work in specimens containing less aluminium, though in a less marked degree.

The microscopic examination of the specimens shows the presence of crystals.

The coefficients of expansion of these crystals are probably different from the coefficient of expansion of the surrounding matrix; and since solidification takes place at a high temperature, the material of the specimens would, at ordinary temperatures, be in a strained condition.

Fig. 4.



The effect of repeated heating and cooling would gradually produce disintegration.

Let us assume that the change in the magnetic condition due to this breaking down of the material of the specimen is, to a first approximation, equivalent to the introduction of an air-gap in the magnetic circuit.

If this were the case, the actual magnetic force in the specimen would be less than that due to the magnetizing-current alone.

Let us assume that, after a certain number of heatings, the only change going on is due to disintegration, and that the actual force in the specimen can be represented approximately by the expression (H−KB) (as would be the case with a split ring), where H = the magnetic force due to the spiral alone, and K is some constant depending upon the number and size of the gaps in the specimen (due to disintegration). If then H_1, H_2 be the values of H on the two curves I and II (fig. 4) corresponding to a given value of B, we should, on the above assumption, have the relation

$$H_1 - K_1B = H_2 - K_2B,$$

where K_1, K_2 are the two values of K for the two curves considered, or

$$\frac{H_1 - H_2}{B} = (K_1 - K_2) = \text{constant}.$$

Hence, on the above assumption, the curve connecting $(H_1 - H_2)$ and B should be a straight line. This curve is shown as III on fig. 4.

It will be seen that this curve differs considerably from a straight line. It is interesting, however, to compare these curves with some obtained by Mr. C. G. Lamb (Phil. Mag. Sept. 1899). Mr. Lamb experimented on a piece of iron first in the form of a bar, and secondly in the form of a ring. The B and H curves for the ring and bar are shown in Mr. Lamb's paper on fig. V. as R and P respectively.

If now H_1, H_2 are the field-strengths corresponding to a given value of B for these two curves, then $\frac{H_1 - H_2}{B}$ should theoretically be a constant, and the curve connecting $(H_1 - H_2)$ and B should be a straight line.

If, however, a curve connecting $(H_1 - H_2)$ and B be plotted from the two sets of observations in question, it will be found to differ from a straight line, and to be very similar in general form to curve III above. Hence it is concluded that the assumption made to explain the change in the permeability of the alloy due to repeated heating and cooling is probably much nearer the truth than the form of curve III would at first sight seem to indicate.

§ VII. *Experiments near the Temperature of Minimum Permeability.*

A third set of experiments were undertaken to trace the changes in the induction (with a constant field) with change of temperature in the neighbourhood of the temperature of minimum permeability.

As mentioned in Part I., an abrupt change in the permeability is observed at a temperature somewhat less than this.

This abrupt change was more marked during cooling than during heating. It attained its maximum value at a temperature of 652° C. with rising temperatures, and at a temperature of 645° C. with falling temperatures.

This small difference of 7° C. might be due to the temperature of the ring lagging behind the temperature of the thermometer. As, however, the heating and cooling were conducted very slowly, the authors believe it to be a true temperature hysteresis effect.

The balance method (described in Part I.) was used in these experiments. This method, which is inapplicable when the permeability is large (except in the case of laminated rings), enables *small* permeabilities to be determined with ease and accuracy.

The curves obtained are shown on fig. 5 and were plotted from the following readings.

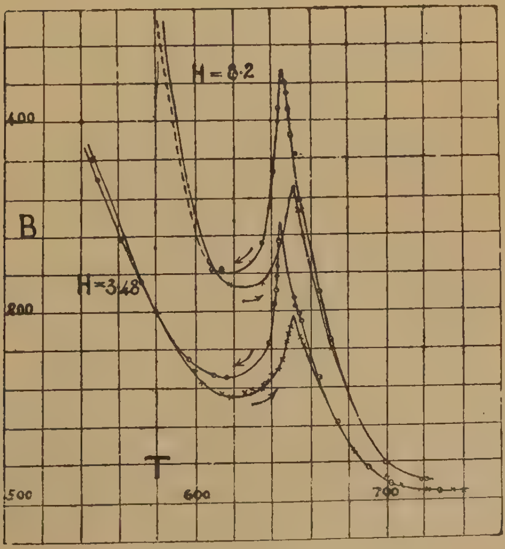
First Series : with rising Temperatures.

H=8·2.		H=3·48.	
T.	B.	T.	B.
584	496	547	360
601	294	580	197
606	262	594	152
619	227	600	136
636	227	604	122
644	258	614	112
650	319	619	108
653	324	626	112
654	303	630	115
656	275	635	116
663	222	637	120
683	97	638	123
697	48	640	130
		643	134
		644	136
		646	147
		648	165
		649	174
		650	179
		655	172
		657	162
		660	148
		666	131
		683	53
		700	21·4
		703	16·9
		708	13·0
		722	7·3
		735	7·1
		741	6·4

Second Series: with falling Temperatures.

H=8·2.		H=3·48.	
T.	B.	T.	B.
721	19·1	741	6·4
719	19·7	728	7·4
700	38·0	702	16·6
671	168	691	32·8
666	218	675	80·5
655	314	667	127·5
652	362	656	187
650	383	655	195
649	411	653	203
648	427	652·5	211
647	439	645	272
644	412	644	250
641	344	643·5	236
635	270	643	220
614	242	642	205
609	243	639	164
		617	129
		610	131
		597	148
		573	230
		562	274
		550	338

Fig. 5.



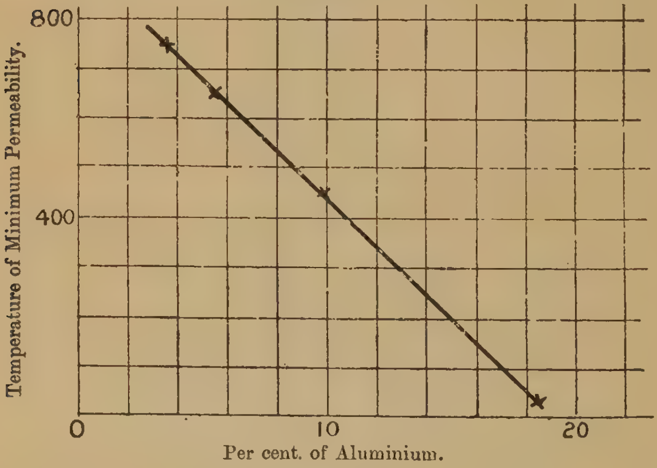
§ VIII. *The Relation between the Temperature of Minimum Permeability and the Percentage of Aluminium in the Specimens.*

It is not possible to say, with any degree of precision, at what temperature the permeability of a specimen attains its minimum value, as the change of permeability with temperature is very gradual in the neighbourhood of the temperature of minimum permeability. It also appears to depend to some extent on the strength of the field considered, being higher for strong than for weak fields.

For the specimens so far investigated the following approximate values of the temperature of minimum permeability have been obtained.

Per cent. of Aluminium	3·64	5·44	9·89	18·47
Temp. of Minimum Permeability ...	750° C.	650°	450°	25°

Fig. 6.



A curve connecting these values is shown as fig. 6. This curve will be seen to be a straight line.

§ IX. *The Microstructure of the Alloys.*

It has been suggested in Part I. that the general behaviour of the alloys might be explained on the assumption that they consisted of crystals surrounded by a solidified mother-liquid.

With a view to ascertaining if this was the case the specimens, after grinding and polishing, were etched with dilute nitric acid and examined microscopically. The eyepiece of the microscope was then removed, and the adjustment was altered until the image fell on the screen of a camera.

When as clear an image as possible was obtained on the screen, a slow plate was exposed for about 15 minutes.

In this way photographs (Pl. VI.) were obtained showing the forms of the crystals in the specimens containing 5·44, 9·89, and 18·47 per cent. of aluminium respectively.

Photograph A. (Specimen containing 5·44 per cent. of Al.) Crystals can be seen in the form of Maltese crosses.

Photograph B. (Specimen containing 9·89 per cent. of Al.) In places crystals having the appearance of a number of rods placed side by side can be seen. Generally the rows are arranged in pairs, the distribution being not unlike that of the bones of a herring.

Photograph C. (Specimen containing 18·47 per cent. of Al.) The crystals are similar to those shown in photograph B; but are larger in size.

The magnification of A and C is about 25 diameters. The magnification of B is about 50 diameters.

An investigation on the magnetic properties of pure alloys of iron and aluminium is now in progress, and we hope very shortly to publish an account of some of the earlier experiments on these purer specimens*.

University College, Nottingham,
June 7th, 1900.

Discussion.

Prof. S. P. Thompson asked if the specimens had been kept for any length of time at a high temperature, because crystals changed and grew in metals at temperatures even far below their melting-points.

Prof. Reinold asked if any specimens had been examined where the crystalline structure had not been observed.

Mr. Blakesley asked if any explanation of the orientation of the crystals could be given.

Dr. Gladstone said it was difficult to know exactly what substances were being dealt with. They might be pure alloys, or mixtures of two or three alloys with iron or aluminium.

Dr. Richardson, in reply, said that the microscopic examination showed that the crystals dissolved in the nitric acid more than the matrix. If a solution could be found which would dissolve the crystals alone, their composition might be determined by analysis.

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* *Vide* Phil. Mag. March 1901.

The impurities undoubtedly affected the phenomena. He had found that the behaviour was different with very pure specimens, and hoped soon to publish an account of further experiments performed at Nottingham. A great deal of work would have to be performed before a satisfactory explanation could be obtained.

LV. *On the Resistance of Dielectrics, and the Effect of an Alternating Electromotive Force on the Insulating Properties of Indiarubber.* *By* A. W. ASHTON, *B.Sc.*, *Royal Exhibition Scholar* [*].

1. IN undertaking the following research an endeavour has been made to ascertain :—

First. What relation exists between the resistance of different dielectrics and the electromotive force at which the resistance is measured.

Secondly. What form is taken by the curves showing the variation of the current with the time when (*a*) a condenser is charged by a battery of given E.M.F., (*b*) the condenser is discharged by placing it directly on to the terminals of a galvanometer.

Thirdly. What effect is produced on the insulating properties of indiarubber by the continued application of a high alternating pressure.

2. The question whether dielectrics can be said to strictly obey Ohm's law in regard to electrical conductivity has been considered by previous observers, but at present very definite conclusions do not appear to have been reached. The variation in the insulation resistance of several cables was examined by Heim (see 'Electrician,' vol. xxv. p. 751). The method of measurement used was that known as the "direct deflexion" method, in which the current is measured by the deflexion of a sensitive galvanometer joined in series with a battery and the plates of the condenser formed by the cable

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[*] Read May 31, 1901.

tested. Readings were taken after one or two minutes' electrification, and after a reading at any one pressure the inner and outer conductors of the cable were connected for one or two hours in order to get rid of the slowly disappearing "residual charge." From these experiments, Heim concluded that the dielectrics tested showed a decided deviation from Ohm's law, the conductivity being greater at the higher pressures. In the discussion on a paper by Preece (see Journal Institute of Electrical Engineers, Dec. 1890), some results were given by Alexander Siemens of tests taken on cables with cores of different materials, viz., guttapercha, indiarubber, and impregnated fibre. The charging pressure was varied over a wide range (from 100 to 1200 Leclanché cells), and it was found that the resistance calculated from the current after one minute's electrification became less as the pressure increased. Leick (Wiedemann's *Annalen*, No. 13, 1898) has tested certain dielectrics, viz., guttapercha, paraffin, and sulphur, and has found an increase of conductivity at the higher voltages.

3. In all the above experiments, the resistance of the dielectrics examined has been calculated from the values of the current obtained at not more than a few minutes' electrification. Unfortunately these values of the current are those which are most affected by the previous electrical treatment of the dielectric. In a paper by Ayrton and Perry, "On the Viscosity of Dielectrics" (see Proc. Roy. Soc. vol. xxxvi.), it is suggested that more accurate values of the true conductivity of a dielectric might be obtained by taking readings of the current when it has become steady. An attempt has been made to examine certain dielectrics by this method in order to ascertain the conductivity at different pressures. In the above paper, Professors Ayrton and Perry also drew attention to the analogy existing between the behaviour of bodies under mechanical stress and that of dielectrics under electrical stress; it is further pointed out that careful distinction must be drawn between that part of the energy absorbed by the dielectric which is afterwards recoverable, and the portion which is converted into heat, and which determines the amount of true conduction taking place. The form of the "residual charge" curves has been examined in the case of glass by Hopkinson (Phil. Trans. vols. clxvi. &

clxvii.). In these experiments the condenser was charged for a definite time and then discharged for an instant. The plates of the condenser were then joined to an electrometer, and readings of the residual potential were taken from time to time. Amongst other results, Hopkinson found that this residual potential was proportional to the exciting potential.

4. In the experiments which are now described these residual charge effects have been examined in the case of several dielectrics by means of curves showing the current (1) when the condenser is charged with a battery having a galvanometer in series with it; (2) when the condenser is discharged by connecting directly to a galvanometer. The examination of rubber for deterioration in insulating properties when subjected to the continuous action of alternating pressure, has been suggested by the failures which have sometimes occurred when rubber has been used as the insulating material for alternating-current mains. The dielectrics upon which experiments have been made are indiarubber, paraffined paper, and mica. The indiarubber tested consisted of three different kinds of sheet-rubber called Nos. 1, 2, and 3, and an " Okonite " cable.

No. 1 consisted of cut sheet ·068 cm. thick. This was darker in appearance and rather less transparent than Para. It cut rather more easily than most pure rubbers and was less tenacious. On keeping it has become quite hard and almost brittle.

No. 2 was pure Para rubber ·051 cm. thick. It was very transparent and very tenacious, and has retained these properties even after keeping for two years.

No. 3 was a vulcanized rubber, white on the surface and dark when cut. It was ·093 centimetre thick.

The cable tested was a 3/18 in., 2760 feet long, insulated to ·208 in. diameter with vulcanized rubber, and having an outer covering of impregnated braid. The sheet indiarubber was made into condensers by fixing tinfoil on each side by means of indiarubber solution made with pure benzene. The tinfoil sheets were 8 in. × 6 in., the dielectric projecting along each edge an inch beyond the tinfoil in order to prevent leakage. Each condenser thus made was placed between two glass plates, a strip of tinfoil being brought out from each sheet to the upper side of the top glass plate in order to make connexion. The surface of the glass was coated with shellac to prevent leakage by condensation of moisture on the glass. The paraffined paper condenser was made of stout notepaper which was first dried in a hot oven and then dipped into melted paraffin-wax. Four sheets of this paper 10 in. × 8 in. were alternated with five sheets of tinfoil, and placed between two glass plates. The condenser was then put between two iron blocks heated to about 85° C., and thus the wax was heated and allowed to solidify and cool down under pressure. The mica used was very pure and transparent, and consisted of sheets $2\frac{1}{2}$ in. × $4\frac{1}{8}$ in. An endeavour was made to form the plates of the condenser by depositing a film of silver on the mica from a solution of silver nitrate and Rochelle salt. By this means, intimate contact would be made between the metal and the mica without the introduction of any other dielectric in the form of a fixing material, or the inclusion of films of air. This, however, was not successful, as out of 30 sheets silvered not one was obtained which would give steady readings when charged with a 100-volt battery. The plates of the condenser were therefore formed of sheets of tinfoil $1\frac{1}{2}$ in. × $3\frac{1}{8}$ in., which were alternated with the mica sheets, and the tinfoil was kept in close contact with the mica by pressure alone. This was effected by holding the condenser between two brass plates which were bolted together by 5/16 in. bolts, the condenser being insulated from the frame by sheet ebonite. The mica condenser eventually used consisted of 13 sheets of mica varying from ·0009 in. to ·001 in. in thickness.

5. The experiments were carried out in the Pender Electrical Engineering Laboratory under the direction of Dr. J. A. Fleming. The measurements of current were made by means of a sensitive Kelvin Astatic Galvanometer of 6057 ohms resistance provided with a shunt-box. The E.M.F. of the battery of small Lithanode cells was measured during the earlier experiments by a Weston voltmeter, but as the current taken by this instrument was sufficient to cause the E.M.F. of the cells to fall during an experiment, a Kelvin electrostatic voltmeter was used instead. The battery, condenser, and galvanometer were connected up to a three-way key in such a way that, with the key in its normal position, the condenser was charged through the galvanometer, and when the

key was depressed the plates of the condenser were connected directly to the galvanometer. The galvanometer was standardized by means of a Crompton potentiometer and standard resistances. In this way the current corresponding to various points on the scale over the whole range used in any particular experiment was determined by reference to the Clarke cell. The " okonite " cable was immersed in a tank of water 3 ft. × 3 ft. × $2\frac{1}{2}$ ft. deep. The two ends of the copper conductor were brought out to a block of paraffin-wax having four mercury cups. To two of the latter the ends of the copper were joined; the other two mercury cups being connected to a Wheatstone-bridge in order that the resistance of the conductor might be measured during an experiment. The volume of water was so great that the variation in temperature was never more than $0^{\circ}\cdot2$ C. during the day, while the resistance of the copper conductor never varied more than 0·2 per cent. in a day. The temperature of the dielectric was taken as a mean between that of the water and that of the copper conductor. To prevent leakage over the ends of the cable, the braid was removed to a length of 2 feet and the surface of the indiarubber kept clean. A Price's guard-ring was also used to test for end leakage. In the mica and paraffined-paper experiments no special precautions were taken to ensure constancy of temperature during an experiment, or to measure the actual temperature of the dielectric, as the experiments were only intended to ascertain whether equations of similar form to those found for the cable would satisfy the curves of charge and discharge for these dielectrics.

6. In the experiments to determine the variation of resistance with pressure, a battery of cells just sufficient to give a readable current was connected to the voltmeter, and at a given time the circuit containing the condenser and the galvanometer was completed. The deflexion of the galvanometer was noted at the end of the first minute, and from time to time afterwards. The current was found to decrease rather rapidly at first, but when electrification had been continued for about an hour it became approximately constant, especially in the case of the pure rubber condensers. The pressure was then raised and electrification continued until the current again became steady, when the pressure was again raised. This was continued for five or six different

pressures, and the values of resistance when the current had become steady were plotted as ordinates, and the corresponding voltage as abscissæ, giving a curve of resistance with pressure. In the case of the okonite cable an experiment was also made in which a series of readings of the current were taken with the pressure increasing in steps to a maximum, and then decreasing in the same steps.

7. In the experiments to determine the form of the curves of charge and discharge from the cable, it was found possible to take readings for three different periods of electrification in one day, the copper conductor being kept "earthed" between successive chargings. In this manner a set of curves of discharge after 5, 10, 40 minutes' charge was taken, the temperature and charging pressure remaining practically constant. The method of procedure was as follows:—The cable having been short-circuited all night, the temperature was determined by measuring the resistances of the cable and the copper thermometer which floated in the tank. Then the E.M.F. of the cells to be used was read on the electrostatic voltmeter, the leads being afterwards disconnected. The cable was then charged for five minutes, and at the end of that time, as shown on the chronometer, the discharge-key was depressed, the galvanometer being short-circuited for the first fifteen seconds of discharge. Steady readings could generally be obtained after 40 seconds; and these were continued by noting on the chronometer the time at which the galvanometer spot passed successive divisions of the scale until the deflexion had fallen to one centimetre. The galvanometer was then standardized at different points over the whole range used, and readings taken of the temperature and battery volts. This was repeated at the end of two hours for 10 minutes' charge, and again at the end of two and a half hours for 40 minutes' charge. On some days two discharges only were taken, viz.: after 20 and 120 minutes' charge. By this means it was found possible to get a set of discharge readings for 5, 10, 20, 40, and 120 minutes' charge, at 200 volts and a practically constant temperature. In these experiments readings were generally taken of the current during electrification; but separate experiments in which electrification was continued for longer periods were also made to ascertain the equations representing the charging current. Readings of

the current both when charging and discharging the mica and the paraffined-paper condensers were also taken in a manner similar to that described above.

8. The curves in fig. 1 show the readings obtained by the method described in section 6 from a condenser made from the rubber called No. 1. Before this experiment was made, the condenser had been dried for some weeks in order to get rid of the benzene used in the solution by means of which the tinfoil was fixed to the rubber. From the curve of resistance with pressure given, it will be seen that this dielectric shows a considerable decrease in resistance as the pressure is increased. A large number of similar experiments, which have been made on this condenser and on three other condensers made from the same rubber, all give curves very similar to that shown in fig. 1. An endeavour was then made to obtain similar curves of resistance from the okonite cable. This cable was first put into the tank on June 1st, 1899, and was kept continuously in the water until the end of July. The results of the experiments made during this immersion are given in the Tables I. & II., and in fig. 2. In the first experiment on July 4th (see Table I.) readings of current were taken at five different voltages, increasing in steps from 52 to 249 volts. After 75 minutes' electrification at 52 volts, the resistance was increasing $\frac{1}{6}$ per cent. per minute. The pressure was then raised to 100 volts, and after 70 minutes' electrification this rate of increase amounted to $\frac{1}{12}$ per cent. per minute. As the experiment proceeds the final reading at each pressure becomes more constant, until at the highest pressure the variation is only $\frac{1}{24}$ per cent. per minute. It will be seen that the steady resistances at the first four pressures do not differ very much, but at the highest pressure, viz. 249 volts, the resistance shows a decrease of $1\frac{1}{2}$ per cent. On July 5th an endeavour was made to compare the curves of resistance with time at 51·1 volts and 197·4 volts. The results are given in fig. 2. Two sets of readings at 51 volts were taken, one before and one after the experiment at 197 volts, the cable being short-circuited for $1\frac{3}{4}$ hours between experiments. The mean of the two sets of readings at the lower voltage is shown for comparison as the broken line above the curve at 197 volts. It will be seen that both sets of readings at 51 volts give values

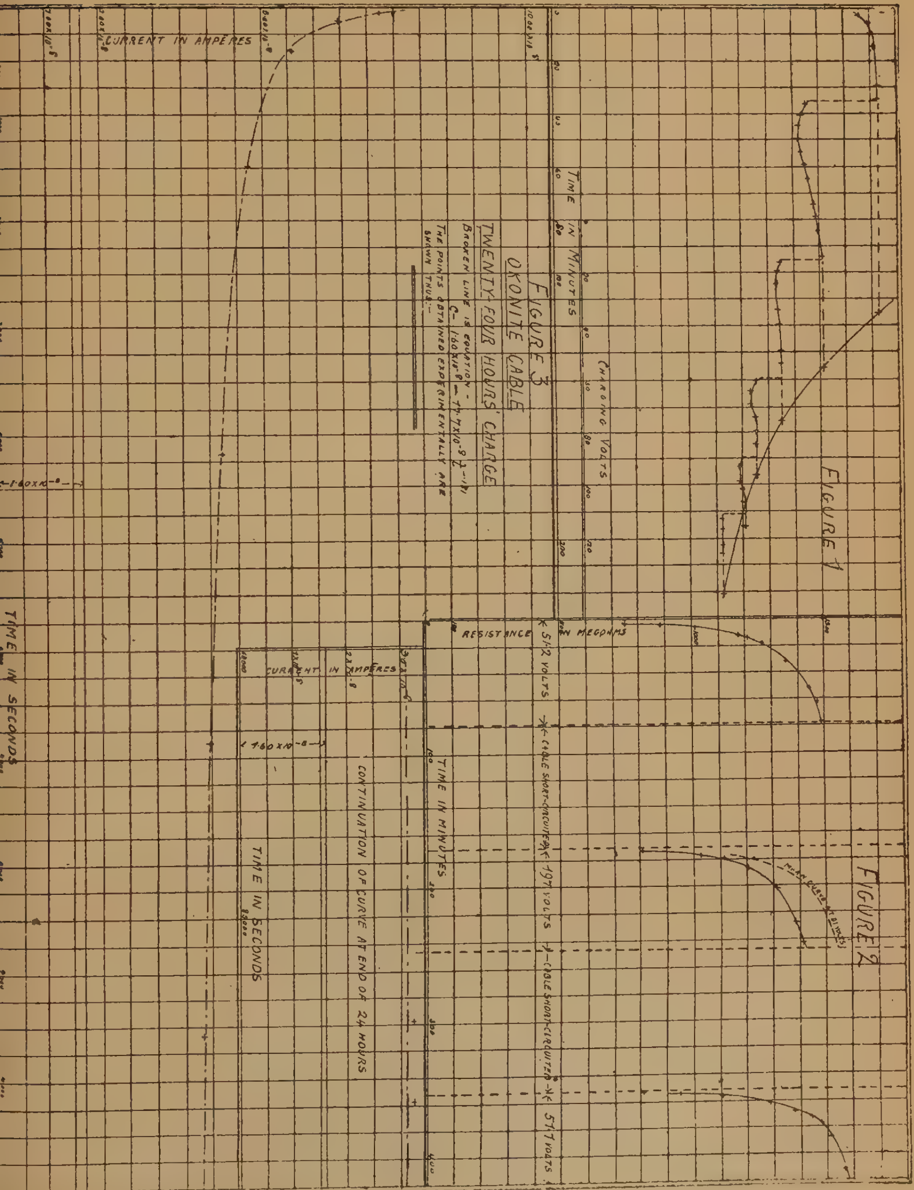
FIGURE 3
OKONITE CABLE
TWENTY-FOUR HOURS' CHARGE
BROKEN LINE IS EQUATION -
$C = 1{\cdot}60\times10^{-8} - 77{\cdot}7\times10^{-8}\,t^{-\cdot171}$
THE POINTS OBTAINED EXPERIMENTALLY ARE SHOWN THUS:-
CURRENT IN AMPÈRES
1·60×10⁻⁸
TIME IN SECONDS
TIME IN MINUTES
CHARGING VOLTS
FIGURE 1
RESISTANCE IN MEGOHMS
51·2 VOLTS
CABLE SHORT-CIRCUITED
197 VOLTS
MEAN CURVE
571 VOLTS
FIGURE 2
CURRENT IN AMPÈRES
1·60×10⁻⁸
TIME IN SECONDS
CONTINUATION OF CURVE AT END OF 24 HOURS
TIME IN MINUTES
100
200
300
400

TABLE I.—Experiment on Okonite Cable, July 4, 1899. Temperature of Bath 18°·3 C.

Time.	Charging Pressure in volts.	Resistance in megohms.	Time.	Charging Pressure in volts.	Resistance in megohms.
11.0	51·4	......	1.50	147·8	1455
11.1	51·4	792	2.2	147 8	1483
11.3·30	...	1035	2.25	147·8	1509
11.4	51·3	1056	2.36	147·8	1525
11.15	51·2	1303	2.39	198·3	......
11.30	51·2	1402	2.40·30	198 3	1260
11.52	51·2	1477	2.42	198	1326
12.14	51·2	1527	2·45	197·4	1388
12.15	100·3	......	3.0	197·4	1457
12.16	100·3	1009	3.21	197·4	1494
12.22·30	100·3	1298	3.33	197·4	1508
12.23	100·3	1306	3.50	197·4	1520
12.30	100·1	1377	3.52	249	......
12·45	100·1	1443	3.54	249	1188
1.1	100	1492	3.57	249	1327
1.21	99·9	1517	4.5	249	1407
1.25	99·9	1522	4.15	249	1449
1.26	148·7	......	4.30	249	1477
1.27·30	148·7	1181	4.48	249	1490
1.29	148·6	1270	5.0	249	1497
1.35	148·2	1383			

TABLE II.—Experiment on Okonite Cable, July 6. Temperature of Bath 19° C.

Time	Charging Pressure in volts.	Resistance in megohms.	Time.	Charging Pressure in volts.	Resistance in megohms.
9.45	51·2		1.15	260	
9 46	51·2	701	1.40	197·6	
9.50	51·2	962	1.41	197·6	1292
9 55	51·2	1057	1.48	197 4	1392
10.6	51·0	1170	1.55	197·4	1380
10.18	50·9	1231	2.10	197·4	1376
10.33	50·9	1271	2.20	197·4	1376
10·49	50·9	1312	2.35	197·4	1376
10 56	50·9	1316	2.40	120·9	......
11.1	121·2	......	2.44	120 9	2135
11.2	121·2	846	2.47	120·7	1934
11.3	121·2	947	2.55	120 7	1736
11.8	120·6	1110	3.20	120 6	1570
11.19	120·6	1207	3.42	120 6	1536
11.40	120 6	1279	3.45	120·6	1536
11·50	120·6	1301	3.46	50·7	current
12.8	120·6	1329	3.47	50·7	negative
12.11	197·4	......	3.49	50·7	" "
12.13	197·4	999	3.51	51·0	12190
12.15	197·4	1096	3.57	51·0	4404
12.30	197·3	1237	4.15	51·0	2596
12.41	197·3	1273	4.50	51·0	2082
12.50	197·3	1288	4.58	51·0	2016
1.8·30	197·3	1312			

of the resistance which are higher than those obtained when charging at 197 volts. On July 6th, an experiment was made in which the pressure was first increased by steps to a maximum and then diminished in the same steps. The values of the resistance so obtained are given in Table II. It will be seen that on dropping the pressure from 197 to 121 volts the current increases as electrification at the lower voltage proceeds, and after 60 minutes gives a nearly constant resistance of 1536 megohms, which is considerably higher than the value which was obtained when the pressure was increasing, viz., 1329 megohms. On the pressure again falling to 51 volts, the current for the first few minutes opposes the charging battery. The resistance calculated from the current after 72 minutes' electrification was 2016 megohms, while the value obtained when first charging at 51 volts was 1316 megohms.

9. The cable was again placed in the tank on November 27th, 1900, and was kept in until the end of the experiments. On December 14th, an experiment was made to determine the curve of charging current. The pressure was kept on for 24 hours, and at the end of that time readings of the discharge current were taken. The results are given in figs. 3 and 7. It will be seen that the observed values of the charging current lie very approximately on the broken line curve which is plotted from the equation

$$c-1{\cdot}60\times10^{-8}=11{\cdot}7\times10^{-8}\,t^{-{\cdot}181}.$$

This equation has been determined by assuming a probable value for the constant to be subtracted from the current readings. If the assumed value be too great, the curve log (c—a constant) plotted to log "t" is concave to the origin, and *vice versa*; the correct value of the constant makes the curve become a straight line. If logarithms of the discharge current be plotted to logarithms of the time which has elapsed since the cable was short-circuited, the points lie on the straight line

$$\log c=-8{\cdot}060-{\cdot}343\log t.$$

The discharge current may therefore be represented by the equation

$$c=87{\cdot}1\times10^{-8}\,t^{-{\cdot}343}.$$

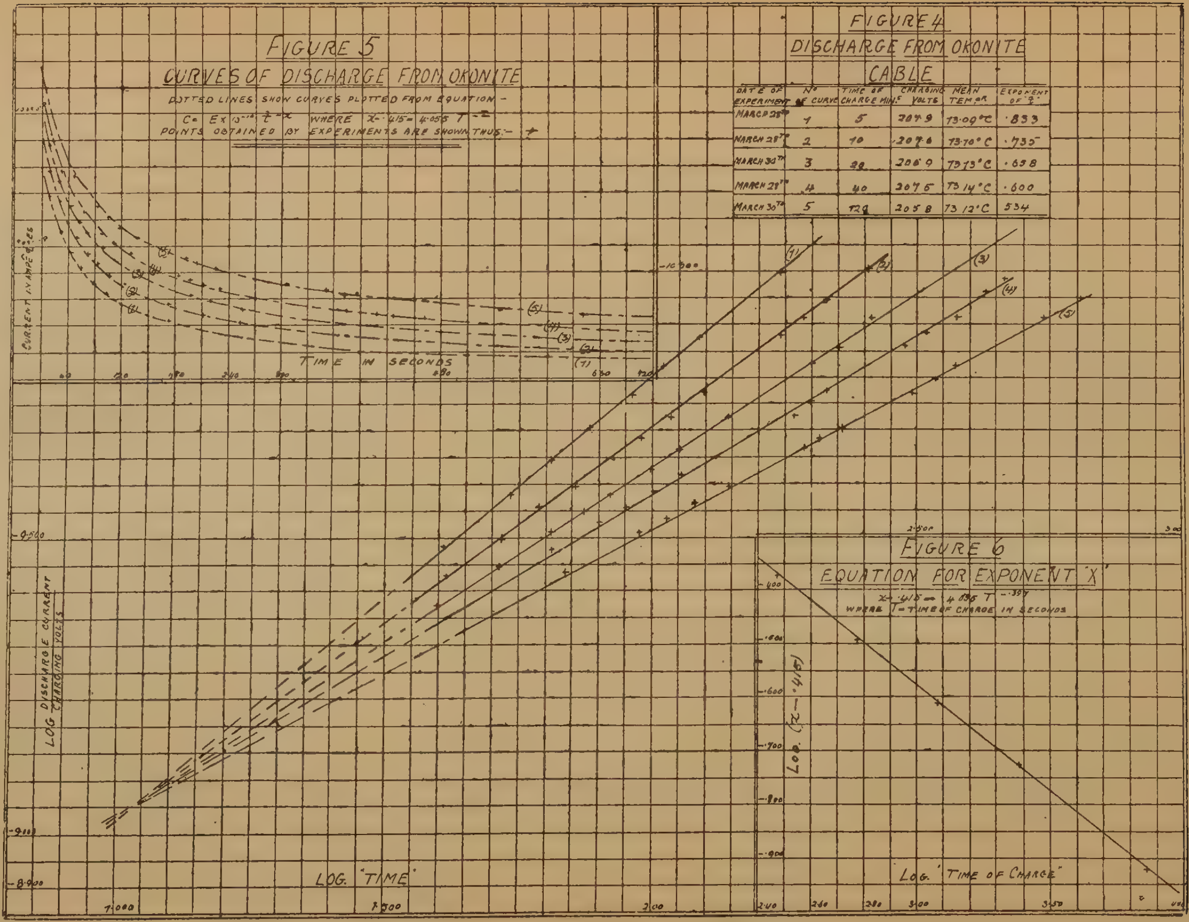

FIGURE 4

DISCHARGE FROM OKONITE CABLE

DATE OF EXPERIMENT	Nº OF CURVE	TIME OF CHARGE MINS.	CHARGING VOLTS	MEAN TEMP.	EXPONENT OF "t"
MARCH 28TH	1	5	207·9	13·09°C	·833
MARCH 28TH	2	10	207·6	13·70°C	·735
MARCH 30TH	3	20	206·9	13·13°C	·658
MARCH 28TH	4	40	207·5	13·14°C	·600
MARCH 30TH	5	120	205·8	13·12°C	·534

FIGURE 5

CURVES OF DISCHARGE FROM OKONITE

DOTTED LINES SHOW CURVES PLOTTED FROM EQUATION –

$C = E \times 10^{-12}\, t^{-x}$ WHERE $x - \cdot 415 = 4\cdot 055\, T^{-z}$

POINTS OBTAINED BY EXPERIMENTS ARE SHOWN THUS:– +

FIGURE 6

EQUATION FOR EXPONENT "X"

$x - \cdot 415 = 4\cdot 055\, T^{-\cdot 397}$

WHERE T = TIME OF CHARGE IN SECONDS

On March 9th two experiments were made. In the first, the cable was charged at 104 volts for 20 minutes, and readings of the discharge current taken; in the second the pressure was 206 volts, the time of charge being the same and the temperature practically constant for the two experiments. The readings obtained are plotted in fig. 8 (p. 733). The index of "t" is ·594 for the first experiment and ·572 for the second; the index being apparently not greatly affected by the charging volts. On March 28th and 30th, a series of five experiments were made in which the temperature remained practically constant, the pressure only varied about 1 per cent. and the time of charge varied from 5 to 120 minutes. In order to correct for the small variation in pressure, the discharge current was assumed proportional to the charging volts, and the values of log $\frac{c}{\mathrm{E}}$ were plotted to log "t," where c = current of discharge, E = charging volts, "t" = time reckoned from commencement of discharge. This is shown in fig. 4, and it will be seen that the points from the five experiments lie on five straight lines passing through the point

$$\log \frac{c}{\mathrm{E}} = -9{\cdot}000,\ \log t = 1{\cdot}040.$$

The points therefore lie on the straight lines

$$\log \frac{c}{\mathrm{E}} + 9{\cdot}000 = -x(\log t - 1{\cdot}040);$$

and the values of the discharge current are given by the equation

$$\frac{c}{\mathrm{E}} = 10 \times 10^{-10}\left(\frac{t}{10{\cdot}96}\right)^{-x}.$$

The values of the exponent x were found to give a straight line when log ($x - {\cdot}415$) was plotted to log T, and the equation for x was found to be

$$x - {\cdot}415 = 4{\cdot}055\ \mathrm{T}^{-{\cdot}397},$$

where T = time of charge in seconds (see fig. 6). From these two equations, by substituting the time of charge and the charging volts for each particular experiment, the five curves in fig. 5 have been drawn, and the points actually obtained closely follow these curves. In Table III. the readings of the current for three discharges are given, the charging pressure being 104 volts and the temperature constant. The current is given by the equation

$$\frac{c}{\mathrm{E}} = 11{\cdot}64 \times 10^{-10}\left(\frac{t}{8{\cdot}65}\right)^{-x}$$

where $$x - {\cdot}43 = 6{\cdot}22\mathrm{T}^{-{\cdot}500}.$$

Table III.—Readings of Discharge from Okonite Cable on April 10, 1900.

5 minutes' Charge.		10 minutes' Charge.		40 minutes' Charge.	
Time in seconds.	Current in Amps. × 10−8.	Time in seconds.	Current in Amps. × 10−8.	Time in seconds.	Current in Amps. × 10−8.
37	3·80	46·5	3·80	40	5·15
49·5	3·04	59	3·25	52·5	4·39
57·5	2·66	71	2·87	67	3·83
70·5	2·30	85	2·49	81	3·45
86·5	1·955	96	2·31	100·5	3·07
Charging volts 103·6. Temp. 13°·83 C.		108	2·12	112	2·88
		125	1·94	127	2·69
		Charging volts 103·6. Temp. 13°·83 C.		143	2·50
				163	2·32
				189	2·13
				Charging volts 103·6. Temp. 13°·83 C.	

The equations are similar in form to those obtained from the experiments on March 28th and 30th, and the constants are of nearly the same value. In fig. 9 are given the readings obtained by charging the okonite cable at 104, 206, and 337 volts. The equations obtained are :—

(1) at 104 volts :

$$c - 3{\cdot}90 \times 10^{-8} = \mathrm{E} \times 32{\cdot}2 \times 10^{-10} t^{-{\cdot}461}.$$

(2) At 206 volts :

$$c - 6{\cdot}30 \times 10^{-8} = \mathrm{E} \times 28{\cdot}2 \times 10^{-10} t^{-{\cdot}422}.$$

(3) At 337 volts :

$$c - 10{\cdot}4 \times 10^{-8} = \mathrm{E} \times 30{\cdot}7 \times 10^{-10} t^{-{\cdot}484}.$$

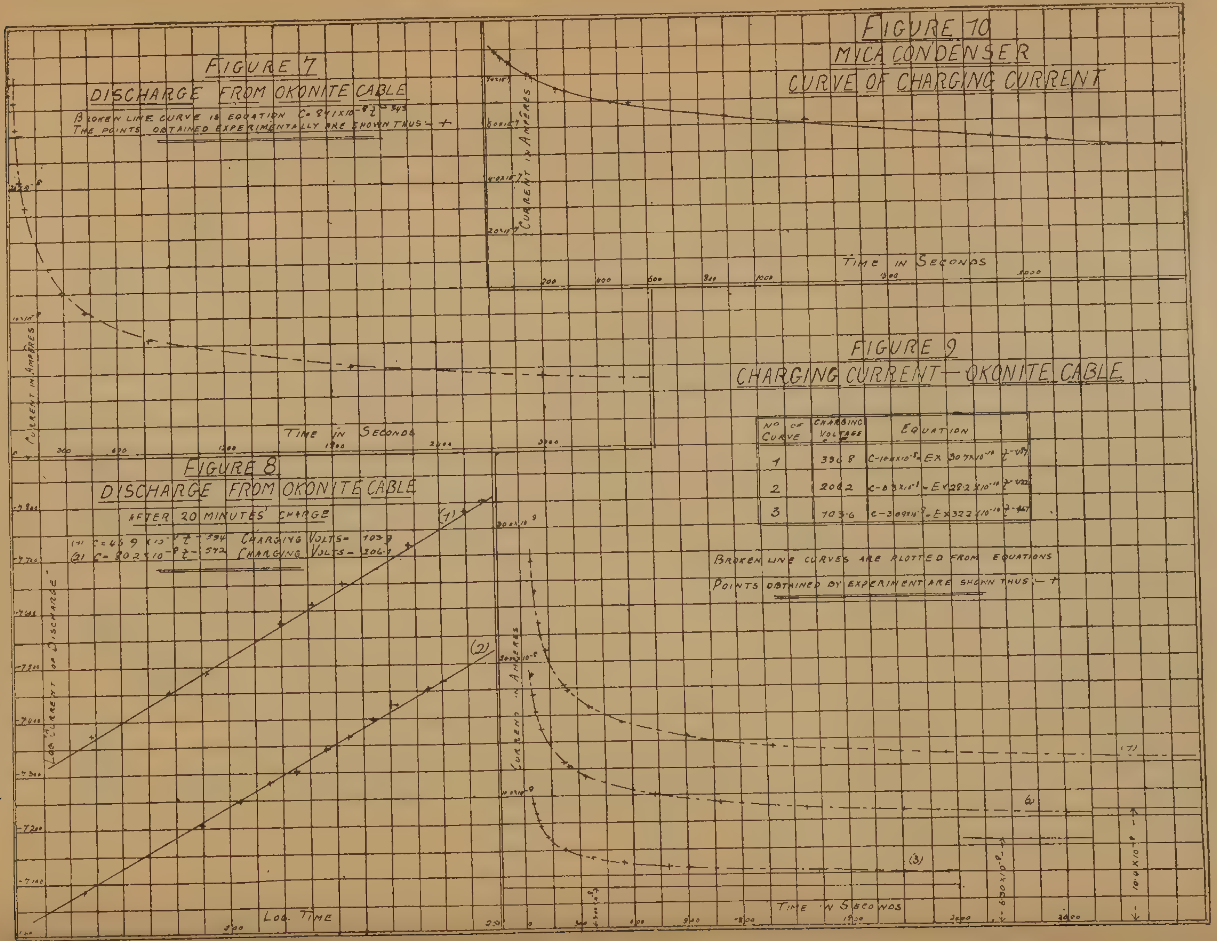

FIGURE 7

DISCHARGE FROM OKONITE CABLE

BROKEN LINE CURVE IS EQUATION $C = 84 \times 10^{-8} t^{-.545}$
THE POINTS OBTAINED EXPERIMENTALLY ARE SHOWN THUS :— +

FIGURE 8

DISCHARGE FROM OKONITE CABLE

AFTER 20 MINUTES' CHARGE

(1) $C = 46 \cdot 9 \times 10^{-8} t^{-.594}$ CHARGING VOLTS = 103·9
(2) $C = 80 \cdot 2 \times 10^{-8} t^{-.572}$ CHARGING VOLTS = 206·7

FIGURE 9

CHARGING CURRENT—OKONITE CABLE

NO OF CURVE	CHARGING VOLTAGE E	EQUATION
1	393·8	$C = 10 \cdot 4 \times 10^{-8} = E \times 30 \cdot 7 \times 10^{-10} t^{-.484}$
2	206·2	$C = 6 \cdot 3 \times 10^{-8} = E \times 28 \cdot 2 \times 10^{-10} t^{-.432}$
3	703·6	$C = 3 \cdot 09 \times 10^{-8} = E \times 32 \cdot 2 \times 10^{-10} t^{-.467}$

BROKEN LINE CURVES ARE PLOTTED FROM EQUATIONS
POINTS OBTAINED BY EXPERIMENT ARE SHOWN THUS :— +

FIGURE 10

MICA CONDENSER

CURVE OF CHARGING CURRENT

TABLE IV.—Summary of Results obtained by Discharging the Okonite Cable.

Date.	Charging Volts.	Temp. ° C.	t=time of Charge in Secs.	Equations.	Exponent of $t-x$.
Dec. 14, 1899.	152·4	13·00	88800	$c=87{\cdot}1\times10^{-8}\,t^{-{\cdot}343}$	·343
Mar. 9, 1900.	103·9	14·15	1200	$c=46{\cdot}9\times10^{-8}\,t^{-{\cdot}594}$	·594
Mar. 9.	206·1	14·21	1200	$c=80{\cdot}2\times10^{-8}\,t^{-{\cdot}572}$	·572
Mar. 12.	104·0	14·21	1200	$c=42{\cdot}6\times10^{-8}\,t^{-{\cdot}578}$	·578
Mar. 12.	205·5	14·21	1200	$c=87{\cdot}9\times10^{-8}\,t^{-{\cdot}584}$	·587
Mar. 28.	207·9	13·09	300	$\frac{c}{\mathrm{E}}=10\times10-10\left(\frac{t}{10{\cdot}96}\right)^{-x}$ where $x-{\cdot}415=4{\cdot}055\mathrm{T}^{-{\cdot}397}$	·836
Mar. 28.	207·7	13·10	600		·734
Mar. 28.	207·5	13·14	2400		·601
Mar. 30.	205·9	13·13	1200		·655
Mar. 30.	205·9	13·12	7200		·534
Mar. 29.	206·4	12·74	1200	$c=90{\cdot}6\times10^{-8}\,t^{-{\cdot}641}$	·641
Mar. 29.	206·4	12·66	7200	$c=67{\cdot}3\times10^{-8}\,t^{-{\cdot}522}$	·522
April 2.	206·9	11·88	300	$c=\mathrm{K}t^{-{\cdot}881}$	·881
April 2.	206·9	11·88	600	$\frac{c}{\mathrm{E}}=9{\cdot}18\times10^{-10}\left(\frac{t}{10{\cdot}9}\right)^{-x}$	·734
April 2.	206·9	11·88	2400		·605
April 5.	206·3	13·94	300	$\frac{c}{\mathrm{E}}=8{\cdot}95\times10^{-10}\left(\frac{t}{13{\cdot}9}\right)^{-x}$	·844
April 5.	206·3	13·91	600		·741
April 5.	206·3	13·90	2400		·574
April 9.	336·7	13·35	300	$\frac{c}{\mathrm{E}}=9{\cdot}82\times10^{-10}\left(\frac{t}{12{\cdot}6}\right)^{-x}$	·874
April 9.	336·8	13·35	600		·752
April 9.	336·8	13·35	2400		·549
April 10.	103·6	13·83	300	$\frac{c}{\mathrm{E}}=11{\cdot}64\times10^{-10}\left(\frac{t}{8{\cdot}65}\right)^{-x}$ where $x-{\cdot}43=6{\cdot}22\,\mathrm{T}^{-{\cdot}500}$	·789
April 10.	103·6	13·83	600		·685
April 10.	103·6	13·83	2400		·560

TABLE V.—Summary of the Results obtained by Charging the Okonite Cable.

Date.	Charging Pressure in volts	Temp. ° C.	Time of Charge in Secs.	Equation.	Resistance.
Dec. 14	152·4	13·00	88800	$c-1{\cdot}60\times10^{-8}=11{\cdot}7\times10^{-8}\,t^{-{\cdot}181}$	9520
Mar. 28	207·5	13·14	2400	$c-5{\cdot}64\times10^{-8}=\mathrm{E}\times29{\cdot}5\times10^{-10}\,t^{-{\cdot}469}$	3680
Mar. 29	206·5	12·75	7200	$c-5{\cdot}20\times10^{-8}=\mathrm{E}\times26{\cdot}3\times10^{-10}\,t^{-{\cdot}451}$	3970
Mar. 30	205·9	13·13	1200	$c--5{\cdot}50\times14^{-8}=\mathrm{E}\times28{\cdot}2\times10^{-10}\,t^{-{\cdot}458}$	3730
April 6	206·2	14·3	4020	$c-6{\cdot}30\times10^{-8}=\mathrm{E}\times28{\cdot}2\times10^{-10}\,t^{-{\cdot}422}$	3270
April 9	336·8	13·4	2400	$c-10{\cdot}4\times10^{-8}=\mathrm{E}\times30{\cdot}7\times10^{-10}\,t^{-{\cdot}484}$	3240
April 10	103·6	13·9	2400	$c-3{\cdot}09\times10^{-8}=\mathrm{E}\times32{\cdot}2\times10^{-10}\,t^{-{\cdot}461}$	3340

The values of the quotient obtained when the constant part of the current is divided into the charging pressure are :—

(1) For 104 volts.—3320 megohms.
(2) For 206 volts.—3270 megohms.
(3) For 337 volts.—3240 megohms.

These values are therefore nearly the same for the three different pressures ; unfortunately the exact comparison is not possible owing to the difference in the temperature of the cable. A summary of the results obtained from the okonite cable is given in Tables IV. and V.

10. The results of experiments made on the mica condenser are given in Table VI. and fig. 10.

Table VI.—Readings of Discharge-Current from Mica-Condenser.

After 60 minutes' Charge.		After 120 minutes' Charge.	
Time in seconds.	Current in Amps. $\times 10^{-8}$.	Time in seconds.	Current in Amps. $\times 10^{-8}$.
35	4·45	38	3·19
45	2·97	48	2·56
55	2·23	58	2·14
67	1·642	68	1·824
75	1·347	76	1·615
		95	1·300
		112	1·091
Charging volts ... 204.		Charging volts ... 97·4	
Equation :— $=10{\cdot}9\times10^{-6}t^{-1{\cdot}155}$.		Equation :— $c=11{\cdot}48\times10^{-7}t^{-{\cdot}983}$.	

Two sets of readings of discharge current are given. The first after one hour's charge at 200 volts, the second after two hours' charge at 97 volts. In both cases the current may be expressed as a power function of the time. The exponent of "t" is $-1{\cdot}155$ for 60 minutes' charge, and $-0{\cdot}98$ for 120 minutes' charge. The readings of current during the charging of the mica condenser are plotted in fig. 10. It has, however, not been found possible to represent the charging current for mica by any equation of form similar to those obtained from the okonite cable. In Tables VII. & VIII. the readings obtained from the paraffin-paper condenser are given. Both experiments were made on June 26th, 1900; the condenser, however, being heated after the first experiment and allowed to cool under pressure as described in Section 4. The charging current in

TABLE VII.—Readings of Current during Charge and Discharge of a Paraffin-Paper Condenser, June 26, 1900.

Charging with 190 volts.		Discharge after 20 minutes' Charge.	
Time in seconds.	Current in Amps. $\times 10^{-8}$.	Time in seconds.	Current in Amps. $\times 10^{-8}$.
40·5	1·938	33	1·726
60	1·514	43	1·403
79	1·303	52	1·197
165	·868	59	1·089
270	·720	75	·878
		87	·773
Equation :— $c-3{\cdot}8\times10^{-8}=28{\cdot}85\times10^{-8}t^{-{\cdot}789}$.		Equation :— $c=33{\cdot}7\times10^{-8}t^{-{\cdot}846}$.	

TABLE VIII.—Readings of Current during Charge and Discharge of Paraffin-Paper Condenser, June 26, 1900.

Charging with 190 volts.		Discharge after 20 minutes' Charge.	
Time in seconds.	Current in Amps. $\times 10^{-8}$.	Time in seconds.	Current in Amps. $\times 10^{-8}$.
45	2·78	38	2·46
58	2·46	48	2·04
220	1·396	55	1·83
300	1·26	63·5	1·62
960	·918	75	1·41
		82	1·304
		90	1·197
		114	·982
Equation :— $c-6{\cdot}0\times10^{-8}=24{\cdot}0\times t^{-{\cdot}630}\times10^{-8}$.		Equation :— $c=54{\cdot}7\times10^{-8}t^{-{\cdot}849}$.	

each case is given by an equation similar in form to those obtained for the okonite cable, and the readings of discharge were also found to satisfy an equation of the form $c=\mathrm{K}t^{-x}$. The value of x for 20 minutes' charge is ·846 in the first case, and ·849 in the second.

11. From the first experiments made on the pure rubber to determine the variation in the resistance with different pressures, it appeared that the current became constant after one or two hours' electrification. If this is so, it is evident that the curves of resistance at different charging pressures can be relied on. In the case of the okonite cable, however, it is evident from the experiments made that the current is still decreasing after several hours' electrification. Therefore the final values of the resistance at each voltage, obtained by increasing the pressure in steps, cannot be taken as a measure of the true conductivity of the dielectric. That the charging current is not quite proportional to the voltage may be seen from the curves in fig. 2. If we take the mean of the two curves obtained with a charging pressure of 51 volts as giving a result comparable with that at the higher voltage, the resistance at 51 volts after one hour's charge is 8 per cent. higher than that after the same electrification at 197 volts.

12. The further experiments on the cable and the paraffin condenser have shown that the charging current may be represented by an equation of the form

$$c-c_0=\mathrm{K}t^{-x},$$

where c=charging current, K and x are constants, and t=time in seconds since electrification commenced. When t is very great, $t^{-x}=0$, and the current becomes constant and equal to c_0. This constant current c_0 may therefore be a current due to true conduction, while the variable part, $\mathrm{K}t^{-x}$, may represent the energy which is being slowly absorbed by the dielectric, and which is given up on short-circuiting the condenser. On this hypothesis, we may call the ratio of the charging pressure to c_0 the true resistance of the dielectric. From the results given in Table V., it will be seen that this resistance, though as high as 9520 megohms on Dec. 14th, 1889, when the cable had been in water for 17 days, had fallen to 3340 megohms on April 10th, when it had been immersed four and a half months. From the experiments of March 28th & 30th, it appears that the discharge current is given by equations of the form

$$c=\mathrm{KE}\left(\frac{t}{\mathrm{K}_1}\right)^{-x};$$

where E = charging pressure, t = time in seconds since the commencement of discharge, and K, K_1 are constants. The exponent x varies with the time of charge and is given by an equation of the form: $x-\mathrm{X}=\mathrm{K}_2\mathrm{T}^{-z}$, where T = time of charge in seconds, and X, K_2, and z are constants. If the time of charge be very great, the term $\mathrm{K}_2\mathrm{T}^{-z}$ becomes zero and $x=\mathrm{X}$, that is, X is the value of the exponent when the charging is continued until the current becomes constant. The above equations have been found to hold for the discharge from T = about 35 seconds, until the current falls to 2×10^{-8} amperes, which is the smallest current readable with any accuracy on the galvanometer. It does not seem probable that these equations would hold for the first half minute of discharge, as, if so, the curves of discharge would cross each other when T = from 8 to 12 seconds. It appears more probable that if readings could be obtained of the discharge-currents from a few seconds after discharge, the five straight

TABLE IX.

Date.	Duration (in seconds) of		Equation for Current.	No. of Coulombs.	
	Charge.	Dis-charge.		Absorbed.	Discharged.
March 28.	2400		$c=61{\cdot}2\times10^{-8}t^{-{\cdot}469}$	$7{\cdot}19\times10^{-5}$	
		66180	$c=87{\cdot}5\times10^{-8}t^{-{\cdot}601}$		$18{\cdot}4\times10^{-5}$
March 29.	1200		$c=62{\cdot}7\times10^{-8}t^{-{\cdot}491}$	$4{\cdot}55\times10^{-5}$	
		11520	$c=90{\cdot}6\times10^{-8}t^{-{\cdot}641}$		$7{\cdot}25\times10^{-5}$
	7200		$c=54{\cdot}3\times10^{-8}t^{-{\cdot}451}$	$12{\cdot}96\times10^{-5}$	
		66360	$c=67{\cdot}3\times10^{-8}t^{-{\cdot}522}$		$28{\cdot}4\times10^{-5}$
March 30.	1200		$c=58{\cdot}2\times10^{-8}t^{-{\cdot}458}$	$5{\cdot}01\times10^{-5}$	
		11940	$c=98{\cdot}8\times10^{-8}t^{-{\cdot}655}$		$7{\cdot}30\times10^{-5}$
			Total......	$29{\cdot}71\times10^{-5}$	$61{\cdot}35\times10^{-5}$

lines shown in fig. 8 would, instead of passing through one point, tend to coalesce into one line as that point is reached.

13. In Table IX. an analysis of the quantities absorbed and discharged by the cable during two days is given. The quantity discharged has been calculated by integrating, for the whole period during which the cable was short-circuited, the equations representing the current. The quantity absorbed has been calculated on the assumption that the variable part of the charging current represents the energy which is being, as it were, "stored up" in the dielectric. It will be seen that the quantity discharged is in each case greater than the quantity absorbed during the corresponding charging. Therefore, if the assumptions made are correct, the dielectric, during these experiments, must on the whole have discharged twice the quantity it absorbed. On the other hand, it may be that all the energy represented by the constant current c_0 is not being converted into heat during the early period of electrification; that is, the true conduction-current increases to c_0 as electrification proceeds. Again, the apparent discrepancy may be explained by the fact that the previous treatment of the dielectric has resulted in the storage of a comparatively large amount of energy which is being given up while the cable is short-circuited, and is augmenting the quantities discharged. In support of this hypothesis, it has been found that dielectrics which as far as could be ascertained had never been subjected to electric stress, have yet given, when joined to an electrostatic voltmeter, an E.M.F. as high as 20 volts (see Note on the Electrification of Dielectrics by Mechanical Means*). The energy thus existing as electric strain in the dielectric is only given up very slowly, especially if the condenser is not kept short-circuited; and it appears possible that the discrepancy noticed in the quantities absorbed and given up by the okonite cable may be thus accounted for. The determination of the true conduction through a dielectric resolves itself into finding the rate of conversion into heat of the electric energy at any instant during electrification. The value of the conduction-current after prolonged electrification would be given by the constant c_0, assuming the equations

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* *Infra*, p. 751.

given above to hold when the time of charge is very great. It does not necessarily follow, however, that, out of the whole current shown on the galvanometer after a few minutes' electrification, c_0 represents that portion which is being converted into heat. We might expect that the rate of conversion into heat would be proportional to the rate of production of strain in the dielectric (see Ayrton and Perry, "On the Viscosity of Dielectrics," Proc. Roy. Soc. vol. xxxvi.): from this it would follow that the true conduction current is greater than c_0 at the commencement of electrification, but decreases to that value as electrification proceeds.

The Alternating Pressure Experiments.

14. The experiments on the effect of alternating pressure on indiarubber were commenced at the Durham College of Science, under the direction of Prof. H. Stroud, and were afterwards continued at the Pender Electrical Engineering Laboratory under Dr. J. A. Fleming. The material tested at Newcastle was a pure rubber very similar to No. 1 (see Section 4), and was made into condensers in the manner described in that section. The preliminary experiments showed that breakdowns under alternating pressure occurred generally at the edges of the tinfoil, and that pale lines of light could be observed round the edges of the tinfoil when under the action of 2000 alternating volts in a darkened room. A set of five condensers, called A, B, C, D, and E, were then made from the same rubber; of these A and B were shellacked round the edges to prevent the discharge taking place from the tinfoil. The condensers were then kept continuously on a transformer giving 2000 volts. When a fault occurred in any condenser, the tinfoil was cut away from the place were the rubber was pierced and the condenser put to the transformer again. The results obtained are given in Table X. Only one condenser showed any great deterioration, viz. C, which after 270 hours continually broke down.

15. The experiments were continued in London, the condensers at first being joined up to a transformer in the Charing Cross substation of the London Electric Supply

Table X.—Results of Alternating Pressure Experiments.

Condenser.	Treatment of edges whether shellacked or not.	Total No. of Hours on alternating pressure.	Total No. of Faults occurring.	Remarks.
A.	Shellacked	1200	1	No discharge observed at edges of tinfoil.
B.	Shellacked	1230	0	No discharge observed at edges of tinfoil.
C.	Not shellacked	270	7	Considerable discharge from edges of tinfoil.
D.	Not shellacked	1300	3	Discharge observed from edges.
E.	Not shellacked	7200	10	Discharge observed from edges.

Corporation, to which Company I am indebted for the gratuitous use of their alternating pressure. During the third year the condensers were subjected to alternating pressure at the Northern Polytechnic Institute. The pressure used in each case was 2600 volts (R.M.S.), but the frequency in the former case was 100 and in the latter case 50.

Three condensers, F, G, and H, were made from No. 1 rubber. The resistance of each condenser was measured before putting on the transformer: they were then submitted to the action of 2600 alternating volts, being only taken off at intervals to measure their resistances. The results obtained are given in Table XI., from which it will be seen that the resistance of these condensers continually increased. The total number of faults occurring in these condensers was three; and as far as could be ascertained the treatment appeared to have no effect on the rubber, with the exception that it became somewhat harder and less elastic. Three condensers, called K, L, and M, were made of No. 2, *i. e.* pure Para rubber. The resistance of all three condensers was very high, being about 200,000 megohms. When subjected to 2600 alternating volts, they all broke down

TABLE XI.—Experiments on Indiarubber under the Action of Alternating Pressure.

Condenser.	Description of Rubber.	No. of Hours on alternating pressure.	Effect of Alternating Pressure.			Result of treating with Ozone for five minutes.
			Resistance.	No of Faults.	General effect.	
F.	From No. 1 (Pure).	3000	Increased from 149 Ω. to 14,000 Ω.	0	No discoloration. No deterioration.	Apparently not attacked.
G.		3000	Increased from 1900 Ω to 200,000 Ω.	2		
H.		937	Increased from 167 Ω to 19,000 Ω.	1		
K. L. M.	From No. 2 (Pure Para).	About 60.	Always very high.	Faults always occurring.	Great discoloration around edges.	Violently attacked. Left in shreds.
N.	No. 3 (vulcanized).	About 60.	Always very high.	Faults always occurring.	Slight discoloration.	Slightly attacked.

within three days, and a peculiar discoloration of the rubber was noticed round the edges of the tinfoil and the outer edges of the rubber. Some chemical action appeared to have taken place, the rubber being discoloured, less transparent, and slightly porous. The tinfoil was cut away from the faults in each condenser, and on again connecting the condensers to the transformer they broke down almost immediately. The discoloration appeared to have advanced still further from each edge, and also appeared round the edges where the tinfoil was cut clear from former faults. The condensers were then put on the transformer a third time with a similar result; no appreciable change in resistance could be detected in condensers K, L, and M. A condenser, N, made from vulcanized rubber No. 3, was also subjected to 2400 alternating volts. This rubber would not stand the pressure very long but broke down twice within 24 hours, the white surface being slightly discoloured round the edges of the tinfoil. All the condensers showed pale lines of light round the edges of the tinfoil when the pressure was applied in a darkened room, and a faint odour of ozone could generally be noticed. An experiment was therefore made to ascertain the amount of decomposition taking place when each kind of indiarubber was exposed to the action of ozone. This was effected by placing the samples in a glass tube leading from an ozone generator through which air was forced, each sample being thus subjected to the action of ozone for five minutes. It will be seen from Table XI. that though No. 1 was apparently not attacked, the pure Para No. 2 was left in shreds.

16. The above experiments having directed attention to the probability of the rubber being attacked by ozone or other gases at the edges of the tinfoil, a condenser was made in which the rubber samples were inclosed between glass plates and were not in contact with the tinfoil. This condenser consisted of two plates of glass kept apart by glass distance-pieces of the same thickness, and having sheets of tinfoil 6 in. × 8 in. fixed to the outer surfaces. This formed a condenser with plates 0·25 in. apart, two thirds of this distance being glass, and the remaining third air-space in which the samples of rubber were placed. The air-space was not sealed up, a limited circulation of air being permitted through the spaces between the glass distance-pieces. After this condenser had been kept continuously on the transformer for a fortnight, a slight discoloration, due to the formation of a buff-coloured powder, was noticed round the edges and on the surface of the samples of No. 2 rubber. This discoloration was also noticed on some samples of pure Para strip such as is used for jointing. This condenser was kept continuously on the transformer for six months, and although the surfaces of samples from No. 2 were almost covered with the buff-coloured powder, no change could be detected in Nos. 1 and 3. Different forms of condenser have been tried for the above test, in which each sheet of tinfoil was inclosed between two sheets of mica ·002 in. in thickness. Two sheets which have been made thus were fixed one on each side of a rectangular framework, cut out of sheet ebonite. In this way the gases evolved at the edges of the tinfoil were

prevented from attacking the rubber, and it was also possible to seal up the samples in the air-space. Experiments were made with condensers of this kind having ebonite 5 millimetres in thickness, (1) with the air-space sealed up; (2) the condenser placed in a sealed bell-jar, the condenser itself not being sealed, but having a space left for the air in the bell-jar to circulate into the air-space of the condenser; (3) with air having free access to the condenser which was not sealed. Each experiment was continued for two weeks, and no action at all appeared to have taken place in experiments (1) and (2), but in (3) the samples of No. 2 rubber showed a slight discoloration on the surface, similar to that observed before with this rubber.

17. From the above experiments it appears that Para rubber, which is the kind generally used in the manufacture of cables, is more easily attacked by ozone or other gas generated by the action of alternating stress on the air, than is the rubber called No. 1. This decomposition has, however, only been detected when there has been comparatively free access of air to the rubber. In the case of the rubber called No. 1, although in the condensers F and G it was very severely stressed, being kept for 3000 hours under an alternating stress having a maximum value of 50,000 volts per cm., no deterioration in insulating properties could be detected; but the fact that this rubber becomes harder and rather brittle on keeping makes it unsuitable for cable-work.

18. The principal conclusions which appear to be justified by the foregoing experiments are :—

(1) That in the case of the okonite cable the current during the first hour's electrification increases as the charging pressure increases.

(2) That this does not necessarily prove the dielectric not to follow Ohm's Law, since the true conduction-current must be considerably less than the total current unless electrification is continued for very lengthened periods.

(3) That in the case of the okonite cable and the paraffin-paper condenser, the charging current is a power function of the time reckoned since electrification commenced, and on this may be superimposed a current of true conduction.

(4) That for the okonite cable, the mica, and the paraffin-

paper condensers, the discharging current is a power function of the time which has elapsed since discharge began; the currents at any particular charging pressure but varying time of charge being given, in the case of the okonite cable by equations of the form

$$c = \mathrm{K}\left(\frac{t}{\mathrm{K}_1}\right)^{-x},$$

where $x - \mathrm{X} = \mathrm{K}_2\mathrm{T}^{-z}$; t=time in seconds since discharge commenced; T=time of charge in seconds; K, K_1, K_2, K_3, and z are constants.

(5) That the only deterioration in insulating properties of indiarubber due to alternating pressure was in the case of pure Para, and appeared to be due, not to any effect of alternating stress on the rubber itself, but to chemical action taking place between the rubber and gases produced by the action of alternating stress on the air.

LVI. *On a Model which Imitates the Behaviour of Dielectrics.* *By* J. A. Fleming, *D.Sc., F.R.S., and* A. W. Ashton, *B.Sc.,* 1851 *Exhibition Scholar* *.

[Plate VII.]

1. It has been shown by Profs. Ayrton and Perry, and by the late Dr. J. Hopkinson and others, that the behaviour of dielectrics with regard to what are termed their "residual charge" effects is analogous to that of wires subjected to mechanical stress. If an iron wire be suspended by one end and a weight applied at the other, it is found that if the application of the weight has only lasted for a fraction of a second, the wire assumes its original length immediately the weight is taken off, provided the stress has not exceeded a certain limit. If the application of the weight is continued for a considerable time, it is found that the wire does not assume its original length immediately the load is removed; a small elongation still remains which slowly disappears, the wire very gradually decreasing in length to its original dimensions.

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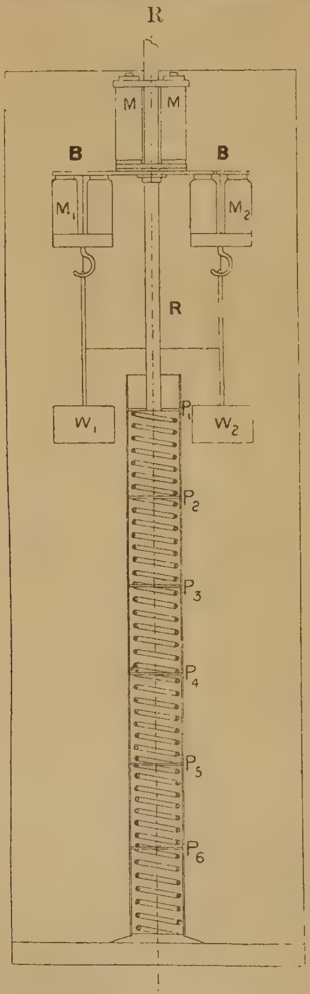
* Read May 31, 1901.

In the case of the condenser, if the time of charge is very short, the whole of the charge disappears almost immediately on the condenser-plates being short-circuited. If, however, the charging pressure is kept on for a considerable time, we have



Front Elevation of Model, with Cylinder in section.

first a discharge taking place immediately on short-circuiting the condenser; and this is followed by a slow giving-up of residual charge causing a continually decreasing current through the short-circuiting wire. The stress on the wire in the mechanical experiment is analogous to the electromotive force in the electrical experiment; the charge of the condenser corresponds to the elongation of the wire. The rate of variation of the charge, *i. e.* the charging or discharging current, is therefore analogous to the rate of change of displacement of the movable end of the wire, that is the velocity of that end of the wire.

2. A simple twisted wire is not, however, able to imitate all dielectric effects. Hence an endeavour has been made to follow up this analogy more completely, and has resulted in the construction of a model from which, by the application of weights, curves of variation of velocity with time can be obtained strikingly similar to the curves of current-variation with time given by condensers when charged and discharged. A simple form of the model can be made by taking two short lengths of spiral spring S_1, S_2, and a metal cylinder slightly larger than the springs in diameter. To each spring is attached a piston P_1, P_2 which just slides in the cylinder. The two springs with pistons attached are placed one above the other in the cylinder, which is then filled with oil. The top piston P_1 must have holes drilled in it sufficiently large to allow the piston to slide very easily through the oil; let W be a weight just sufficient to compress S_1 and S_2 to half their original length. If the weight be applied momentarily, compression is produced in the upper spring S_1; but provided the weight is immediately removed, the compression of S_2 is infinitesimal. If, however, the weight is kept on, the upper spring S_1 is soon compressed to its full extent; but the compression of S_2 proceeds very slowly and with decreasing velocity. If the weight is removed, S_1 regains its original length almost immediately, but the piston P_2 moves up to its original position very slowly. The variation of the displacement of P_1 is therefore very similar to the variation in the quantities absorbed and discharged by a condenser when both the charging and discharging are continued for a considerable time.

3. A simple apparatus such as that described above would draw curves somewhat similar to those obtained from the model about to be described; but it is evident that these

curves would not completely represent the behaviour of a condenser. For the motion of P_1 after the first few seconds of discharge is simply a copy of the motion of P_2; also the motion of P_2 at any instant depends solely on the amount of compression in S_2 at that instant. Therefore it follows that, the springs having been compressed to a given extent and released, the motion of P_2, and therefore of P_1 also after the first few seconds, depends only on the amount of the displacement, and not on the manner in which that displacement was produced. Thus it will be seen that only one velocity-curve could be obtained from this model, and the equation of the curve would not vary with the time of charge. It has been found that if as many as six pistons and springs are used the curves drawn by the model may be represented, at least approximately, by equations which are similar in form to those obtained by experiments on dielectrics. In the model now described the springs are $2\frac{3}{4}$ inches long, made of No. 12's S.W.G. brass wire, with a pitch of about ·3 inches. To each spring is fixed a brass disk which forms the corresponding piston. The piston P_6 fits fairly tight in the cylinder (see figure), and has no hole drilled in it. The second piston has no hole bored in it, but fits slacker in the cylinder than the first. The third piston has one hole $\frac{3}{32}$ inch in diameter, and each succeeding piston has a greater area cut away, the top piston having just sufficient metal left to make the spring come to rest without vibration after being compressed. The cylinder is filled with a mixture of machine-oil and vaseline. To the top piston is attached a brass tube to which is fastened a compound crossbar B. The latter is built up of two pieces of soft iron separated by a piece of sheet brass. The upper part of the crossbar forms the armature of an electromagnet M, the yoke of which has a hole drilled in it to form a guide for the rod R. Two electromagnets M_1 and M_2 carrying weights W_1 and W_2 can be attached to the lower plate of the crossbar, and can be instantaneously detached by breaking the circuit. The upper magnet M, by its attraction of the upper plate of the crossbar, keeps the top piston in its zero position. The magnets M_1 and M_2 being attached, on breaking the circuit of M the crossbar moves downward under the action of the weights, and this corresponds to the charging of the condenser. If the circuit of M_1 and M_2 is now broken, the crossbar moves under the action of the springs alone, and its motion corresponds to the discharge of the condenser. In order to draw diagrams of the motion, a pencil which runs in a guide is attached to the crossbar. This pencil moves over the surface of a clockwork-driven recording-drum which runs in bearings attached to the back of the teak framework of the model.

4. A typical diagram drawn by the model is shown in Pl. VII., fig. 1; the ordinates represent displacement of the crossbar, and abscissæ represent time in arbitrary units. On applying the weight to the crossbar the latter first moves down very quickly, as shown by the steep initial portion of the curve in the diagram. This is followed by the more gradual compression of the lower springs, the crossbar moving with gradually decreasing velocity. At the point B on the curve the weights were detached from the crossbar, and the subsequent motion which is due to the springs alone corresponds to the discharge. It can be seen from the curve, that a large portion of the compression of the springs is given up almost immediately on releasing the weights; the crossbar then moves to its zero position with gradually decreasing velocity, due to the lower springs recovering their original length very slowly. In fig. 3 the velocity-curve obtained by differentiating curve I. is given. The general form of this curve is very similar to the current-curve one might expect to obtain when charging a condenser; but in the later parts of the curves the accuracy with which the model imitates the results obtained from actual dielectrics is very striking. In figs. 2 and 4 logarithms of the velocity are plotted to logarithms of the time of charge or discharge, and in each case the points so obtained are very nearly on straight lines, showing that the velocity of the pencil both when charging and discharging is a power-function of the time. Both these results have also been obtained by one of us in experiments on dielectrics. The three diagrams given in fig. 1 show the effect of varying the time of charge. From the equations obtained for the velocity of the pencil (see fig. 2) it appears that the exponent of t in the equations of discharge decreases as the time of charge increases, a result which has been shown

to hold in the electrical case. The diagram in fig. 6 has been given to illustrate the action of the model in imitating the production of a second discharge which takes place when a charged condenser, after being once short-circuited and then kept insulated for a period, is short-circuited a second time.

5. The production of successive sparks from a charged leyden-jar is a very familiar fact. This can be imitated by the model. During the earlier part of the first discharge the upper springs extend to their full length, and while the lower springs are still considerably compressed and if the crossbar is then clamped, a state equivalent to insulation commences. The extension of the lower springs, however, still continues; but as the crossbar is fixed this results in the compression of the upper springs. When the crossbar is again released a second discharge takes place which is weaker than the first; if the operations be repeated, further discharges can be obtained until the crossbar returns to its zero position. In fig. 5 a diagram is given to illustrate the effect of decreasing the charging pressure of a condenser. This was obtained from the model by breaking the circuit of the magnet M_1 only, and allowing the pencil to move under the action of M_2. It will be seen that the effect of thus lowering the pressure is to cause a variation in the discharge to take place, similar in form to that in the corresponding electrical cases. It is interesting to consider also the effect of temperature on the discharge as given by the model. Increased temperature would make the mixture of oils in the cylinder become less viscous. This would cause the crossbar, when moving under the action of any given weight, to have a greater velocity, especially at the later portions of the discharge and discharge curves. This agrees with the fact that when the temperature of a cable increases, the charging and discharging currents as given by a galvanometer also increase. By freezing a portion of the oil, the effect of very low temperatures on dielectric constants could be imitated. It is evident, therefore, that in many ways the characteristic properties of dielectrics can be illustrated by experiments with a model of this kind, which will, it is hoped, afford valuable help in illustrating the behaviour of dielectrics.

The question may be asked, In what respect the action of this model differs from that of a simple twisted wire as an illustration of dielectric effects? The answer is that experiment has shown that although the current flowing out of a charged condenser is a simple power-function of the time, yet the exponent varies with the time of charging.

In the case of the simple twisted wire, whether the wire is twisted quickly or slowly, the twist per unit of length of the wire is approximately the same.

In the case of the model here described, it is evident that the effect on the compression makes itself felt first on the top piston; and hence that the amount of total compression depends not only upon the compressing force, but upon the time during which this acts, and that this compression is propagated gradually down the chain of pistons. In this respect the model imitates closely the electrical behaviour of dielectrics such as indiarubber when subjected for various times to different electromotive forces.

In the above model the velocity of return of the upper piston to its zero position is very approximately represented in terms of the time t reckoned from the instant of release by an equation of the form

$$V = Ae^{-Bt},$$

where A is a constant, and B is a function of the time T during which the operation of compression lasted.

In the case of the charge and discharge of a condenser, an equation of the above form has been shown by one of us to connect the value of the discharge-current and the times of discharge and charge.

LVII. *Note on the Electrification of Dielectrics by Mechanical Means.* By A. W. ASHTON, *B.Sc.*[*]

THE apparatus used consisted of two brass plates P_1 and P_2, the upper one, P_1, being 6 inches diameter and ·25 inch thick. These two plates were connected to a quadrant electrometer, E. The electrometer gave a deflexion of 4·72 cms. for one volt. The sheet of rubber was laid on P_2, and P_1 was laid gently on top of the sheet. The first sheet tested was pure Para rubber, which had been rolled to a thickness of ·012 inch, and had not previously been electrically treated. The deflexion of the electrometer was about 5 cms., but on joining P_1 to P_2 this disappeared. A 2-lb. weight was then dropped on P_1 from a height of three inches. The spot of the electrometer moved very quickly off the scale to the right, but immediately returned and settled down to a fairly steady deflexion to the left. The electrometer thus appeared to receive two impulses, of opposite sign, one quickly following the other. It appeared probable that the first impulse might be due to the compression of the sheet, and the second to the extension of the dielectric when it recovers its original thickness. To test this, the sheet was stretched transversely and the effect on the electrometer noted. A fresh sheet of rolled Para rubber was taken, ·022 inch in thickness, and placed on the plate P_2. The top plate P_1 was then gently placed on the sheet of dielectric. The electrometer showed a deflexion of 5·0 cms. to the right, and the deflexion was slowly increasing. This was due either to the compression produced by the top plate, or to the mechanical stress to which the dielectric had been subjected during manufacture. The two edges of the rubber sheet were then grasped gently in the hands, and the sheet stretched until its length

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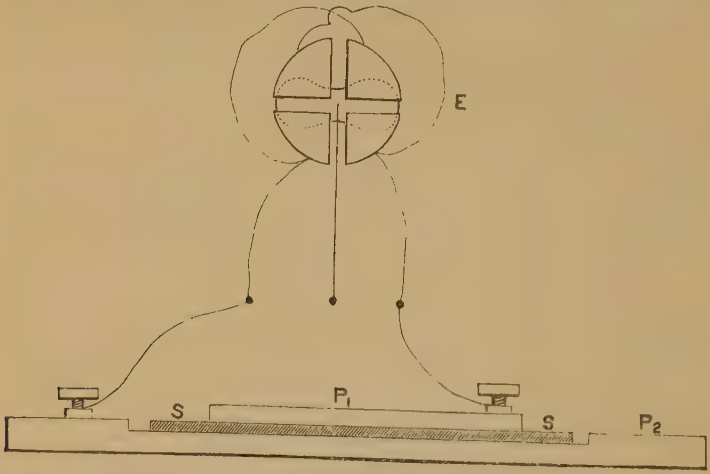
[*] Read May 31, 1901.



increased about 30 per cent. This caused the electrometer-spot to fly off the scale to the right, showing a difference of potential of at least 7 volts established between the plates, the top plate being negative. The condenser and electrometer were then discharged for an instant, the sheet being then released and allowed to return to its original dimensions. This caused the electrometer-spot to fly off the scale to the left, showing the top plate to be positive, the E.M.F. being more than 10 volts. The sheet of dielectric was then reversed, and exactly the same effect produced, viz. extension made the top plate negative, and *vice versa*. It appears, therefore, that polarization of a dielectric may be produced by simple pressure or extension, and hence some part of the mechanical energy expended on the indiarubber during manufacture may remain in the dielectric as electric energy.

DISCUSSION (*on preceding three papers*).

Prof. AYRTON said he would like to know in what respect the model shown was superior to a strained wire. He had noticed about ten years ago that alternating E.M.F.'s appeared to improve condensers. He was then working with comparatively small voltages, and he was interested to know that Mr. Ashton, working with high voltages, had established the improvement. The deflexion obtained by stretching the indiarubber sheet might be due to changes in temperature, the dielectric having a high thermoelectric power.

Mr. PRICE was glad that the question as to what actually might be called the resistance of a dielectric had been raised. There are two theories of residual charge; one due to Maxwell and the other to Heaviside. The model exhibited represents Maxwell's theory. He considered that the electrometer experiment with the rubber dielectric favoured Heaviside's theory; that is, that the dielectric is composed of small charged bodies similar to the small magnets conceived to constitute a magnet. He expressed his interest in the fact that the top plate of the condenser was always negative.

Mr. BLAKESLEY suggested putting a small hole in the bottom piston of the model so that it might represent a condenser passing a small steady current. With regard to the stretched rubber experiment, he said it would be interesting to make observations with the plates of the condenser vertical.

Mr. CAMPBELL said that, since reading the paper, he had tried the effect of applying pressure to an indiarubber condenser in series with a 100-volt battery and an electrostatic voltmeter. The small increase of deflexion obtained might be explained by the change in capacity (of the condenser) which here masks the real effect.

Mr. APPLEYARD said it was important to have perfect contact between the dielectric and the metal plates.

It was pointed out by a visitor engaged in the cable industry that manufacturers are aware that pressure affects the insulating properties of gutta-percha. Rubber is a mixture, and different rubbers behave differently under the action of alternating potential-differences.

Prof. THOMPSON said that if the quantity of electricity taken in on charging was equal to the quantity given out on discharge, then there could be no dielectric hysteresis.

LVIII. *The Mechanism of Radiation.* *By* J. H. JEANS, *B.A.*, *Scholar of Trinity College, and Isaac Newton Student in the University of Cambridge**.

Introduction.

§ 1. THIS paper attempts to give a consistent interpretation of a certain class of phenomena by referring them all to the same hypothetical view as to the structure of matter. As the result of some work on the kinetic theory of gases the author was led, rightly or wrongly, to the conclusion that the kinetic-theory phenomena of matter compel us to attribute certain definite properties to the molecules of which matter is composed. The range of view as to the structure of matter could, it was found, be still further narrowed by the help of certain optical phenomena. It was then of interest to examine to what extent the view arrived at in this way was capable of giving an account of the remaining phenomena, and how it compared in this respect with other views as to the structure of matter.

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* Read June 14, 1901.

To this end, several hypotheses as to the structure of matter were examined by the present writer, and it seemed to him that the one which is put forward in this paper was much more capable of giving an account of the phenomena in question than were any of the others tested by him. For the sake of brevity, it has been thought advisable to remove the scaffolding, by the help of which the theory of the present paper has been formed, and simply to submit for judgment the view ultimately arrived at, together with the account of the phenomena of matter to which it leads, in so far as it has been found possible to examine these phenomena.

The theory will not, it is hoped, be judged as an attempt to attain to ultimate truth. At most the author hopes that by attempting a definite and consistent hypothetical interpretation of certain phenomena, some kind of clue may be suggested as to the real significance of these phenomena, and perhaps something of the nature of a foreshadowing of the real truth arrived at.

Analytical Expression for the Radiation from a Gas.

§ 2. It will be best to begin by a consideration of the general question of spectroscopy.

We shall suppose the radiation emitted by a gas to be the aggregate of contributions from a great number of similar vibrators. Each of these vibrators will be supposed to be capable of vibrating with certain definite frequencies of vibration, and the disturbances of the æther which are set up by these vibrations constitute the radiation.

Let us, in the first place, consider only the radiation propagated along a certain line of sight, say the axis of x, and polarized in a certain plane, say that of xy. If the vibrator were at rest in space, this radiation might be represented, so long as the vibrator was undisturbed by collisions, by

$$A \cos (pt + \epsilon),$$

in which A and ϵ would be constants, which would, in general, depend upon the orientation of the vibrator.

If, however, the vibrator is rotating with an angular velocity w about some axis fixed in space, the above expression will no longer represent the radiation in question. This radiation may, however, be represented by

$$\mathrm{A} \cos pt + \mathrm{B} \sin pt,$$

where A, B are themselves periodic functions of the time, of period $2\pi/w$.

If we expand A and B in Fourier-series, the foregoing expression can be at once expressed as a series of simply harmonic terms of frequencies

$$p, \quad p \pm w, \quad p \pm 2w, \ldots \&\text{c.}$$

Suppose, to take a particular case, that the vibrator is an electrical doublet of strength A cos pt, rotating about a fixed axis with angular velocity w, the axis of the doublet always making a constant angle with this line. The direction-cosines of the axis of the doublet at time t are each of the form

$$a + b \cos (wt + \eta),$$

so that the component of the doublet along any axis is of the form

$$\mathrm{A}\,(a + b \cos (wt + \eta)) \cos pt,$$

and this may be replaced by three simply harmonic doublets of frequency

$$p - w, \quad p, \quad p + w$$

Hence the radiation in question may be represented by three simple harmonic terms of frequencies

$$p - w, \quad p, \quad p + w.$$

Analysed in a spectroscope, this radiation will show bright lines at the points corresponding to the frequencies p, $p \pm w$, and (in the more general case) $p \pm 2w$, &c. In adding up the radiation from all the vibrators, we must suppose w to vary as we pass from vibrator to vibrator, so that the whole radiation may be supposed to consist of two parts.

(α) A bright line at the point of the spectrum corresponding to the frequency p.

(β) A band of light, symmetrical about the point p, and of which the width depends upon the mean rotation of the vibrators.

§ 3. The complete spectrum is, of course, found by adding up the radiation corresponding to every degree of vibratory freedom. The condition that the resulting spectrum shall be a pure line-spectrum, is that that part of the spectrum which has just been denoted by β shall be imperceptible. This condition can be fulfilled in two different ways:—

(i.) The intensity of the bands of light may be very small in comparison with the intensity of the bright lines.

(ii.) The breadth of these bands may be so small that they are indistinguishable from the lines.

§ 4. Let us begin by the consideration of the former alternative. The aggregate brightness of a band bears to that of a line a ratio comparable with unity except when the radiation emitted by a vibrator is approximately the same in all directions. Now spherical symmetry of this kind would be at variance with the fundamental suppositions of the undulatory theory, for spherical symmetry could only be obtained by supposing the radiation to be specified by a single vector, and this vector to be radial at every point; whereas the undulatory theory is such that two vectors are required to specify the radiation, and these vectors, being perpendicular to one another, cannot coincide in direction.

§ 5. We fall back, therefore, upon the second alternative, and inquire what is the condition that the bands shall be so narrow as to be indistinguishable from the lines. The condition is obviously that the mean value of w shall be very small in comparison with p.

Now in the case of a molecule of a gas, the mean energy of rotation about a principal axis which is not an axis of symmetry is equal to one-third of the mean energy of translation. If k_1, w_1 are the radius of gyration and the rotation about such an axis,

$$\kappa_1{}^2 w_1{}^2 = \tfrac{1}{3} c^2,$$

where c is the velocity of translation, and mean values are taken on each side of the equation. We therefore find that the mean value of w is of the order of c/κ. If, in C.G.S. units, we take $c = 5 \times 10^4$, and $2\kappa = 10^{-9}$, we get $w = 10^{14}$.

The value of p is of the order of 3×10^{15}, so that in this case p and w are of the same order of magnitude, and the bands of the spectrum cannot be so narrow as to be indistinguishable from lines. This shows that the vibrator, at any rate in the case of a gas emitting a line-spectrum, is not identical with the molecule.

§ 6. An exception, however, occurs in the case of monatomic gases, and this seems to supply the key to the situation. In a monatomic gas the energy of rotation is known to be very small in comparison with the energy of translation, so that, in our notation, w is small compared with p. We should therefore expect a monatomic gas to emit a pure line-spectrum.

In general, the condition that w shall be small in comparison with p is, that the rotating body shall be so nearly spherical in shape that the rotation never attains to a value comparable with that which the Boltzmann law of the partition of energy would assign to it. In this case, the energy of rotation is proportional to what has been, in a former paper*, designated as a "subsidiary" temperature. This temperature is given by an equation of the form†

$$\tau = \rho f(\mathrm{T}),$$

where τ is the subsidiary temperature, proportional to the mean value of w^2, ρ is the density of the gas, and $f(\mathrm{T})$ is a function of the temperature of the gas, of which the value is very small.

§ 7. We are therefore driven to the conclusion that the vibrators by which radiation possessing a line-spectrum is emitted, must behave like the molecules of a monatomic gas. In other words, we are led to suppose that a line-spectrum is emitted only by the dissociated atoms of a gas and not by the complete molecules, and, further, that these dissociated atoms must be spherically symmetrical.

§ 8. On this view, we can see why it is that pure line-spectra are emitted only by elements, and not by compounds. We can also understand why a gas raised to incandescence by mere heating emits a continuous and not a line-spectrum:

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* "Distribution of Molecular Energy," Phil. Trans. cxcvi. p. 397.

† *L. c.* p. 30.

the vibrations must be those of complete molecules, not of dissociated atoms. The same substance placed in a flame emits its line-spectrum at a temperature lower than that at which it first becomes luminous if merely heated. Hence the dissociation and radiation which occur when a substance is placed in a flame, cannot be merely the result of the temperature of the flame : they must be produced by chemical action, a view originally put forward by Pringsheim*.

The faint continuous spectrum which is often seen to accompany a line-spectrum must be supposed to proceed from undissociated molecules.

We have incidentally found a factor tending to increase the width of the lines, namely, the rotation of the atoms by which these lines are emitted. We must, however, consider this question at greater length in a later section (§ 34).

The Electrical Structure of an Atom.

§ 9. Let us now leave this train of thought altogether, and regard an atom as a collection of negative and positive ions, the negative ions each carrying a charge of electricity of amount $-e$, and the positive ions each carrying a charge $+e$.

The conception of an atom which we are tempted to adopt at first sight, is that of a collection of point charges of positive and negative electricity, these charges repelling or attracting according to the law of the inverse square of the distance. These point charges would be supposed to settle into a position of stable equilibrium, and the oscillations about this position might be supposed to be the vibrations of definite period which result in the emission of a line-spectrum.

Against this very simple conception of an atom there is one fatal objection : Earnshaw's theorem shows that no position of stable equilibrium exists. It is not hard to see that positive and negative charges would rush together and annihilate one another until there would be nothing left to distinguish the point at which a body ought to be from a point in empty space. In fact a consideration of the physical "dimensions" of the quantities concerned, will show that there could be nothing to determine the linear scale of the atom *.

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* Wied. *Ann.* xlviii. p. 428 ; xlix. p. 347. On the luminosity produced by heating, see J. Evershed, Phil. Mag. xxxix. p. 460 ; A. Smithells, Phil. Mag. xxxvii. p. 245, and xxxix. p. 122 ; A. Paschen, Wied. *Ann.* l. p. 409.

§ 10. An escape from this dilemma is for the moment made possible by supposing the stability of an atom to be kinetic rather than statical, but this seems (to the present author at least) to lead to a new and apparently insurmountable difficulty. There will be an infinite number of steady motions possible, and a different series of vibrations will be possible about each state of steady motion. The periods of the vibrations, then, will not form a spectrum of disconnected lines, but of continuous bands. We cannot suppose the ions in an atom to be oscillating about a state of steady motion which is the same for all atoms, for even if the atoms were once arranged in this special state, they would rapidly depart from it under the influence of collisions. To explain the line-spectrum of an element, it would be necessary to suppose that the vibrations by which it was produced were not vibrations of the ions as rigid bodies, but vibrations internal to the ions, and, moreover, vibrations which do not depend on the configuration of ions in the atom. If this is the true account of the origin of the line-spectrum, it is very hard to see why the spectra of different elements are not all the same. Further, the ratio of the charge of an ion to its mass, which is deduced from the magnitude of the Zeeman effect, on the assumption that the spectral lines arise from bodily vibrations of the negative ions, is in close agreement with the actual value of this ratio ; and this fact supplies a powerful argument against supposing that the lines of the visible spectrum arise from vibrations of units smaller than the negative ion.

§ 11. A second way of escape from the dilemma of § 9 is opened by supposing that the ions are not strict point charges, but that in some sense they possess size. In this case the law of force will not be that of the inverse square at all distances. The law of the inverse square will require correction at distances comparable with the size of an ion, so that two ions of opposite charge will not necessarily rush together and annihilate one another, and the objection of § 9 falls through.

For this explanation to hold, it is necessary that two ions should repel one another at very small distances, independently

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* *Cf.* Larmor, Æther and Matter, § 122.

of their sign, and this shows that the force cannot be proportional simply to the product of their charges.

Instead of supposing the complete potential-function to be

$$\frac{ee'}{r},$$

we are compelled to suppose it to be of the form

$$ee'\psi_1(r)+mm'\psi_2(r),$$

where ee' are the charges, and mm' the masses of the two ions*. When $r=0$, we must have

$$\psi_2(r)=\infty, \quad \text{and} \quad \psi_2(r)/\psi_1(r)=\infty.$$

When r is very great we must have, in the limit,

$$\psi_1(r)=r^{-1}, \quad \psi_2(r)=0\ †.$$

This complete potential-function must necessarily contain a reference to some fixed length or lengths ‡, and this will determine the scale of the atom. Let us suppose the potential-function to be such that some stable configurations of ions exist, and examine the consequences of regarding such a configuration of ions as our picture of an atom. Seeing that there are several hundreds of ions in an atom §, we should naturally expect the configuration of stable equilibrium to be such that the shape of the atom is very approximately spherical, and this conclusion agrees with the result already reached in § 7.

The Equations of Small Displacements of the Ideal Atom.

§ 12. To determine the positions of equilibrium and the vibrations about these positions, for a dynamical system con-

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* For ions such as we are now considering $e=\pm e'$ and $m=m'$ I have, however, stated the law in general terms.

† In an exhaustive treatment of æther-force, $\psi_2(r)$ would probably be identical with the gravitational potential, but for our present purpose gravitational forces may be disregarded.

‡ *E.g.* we might have as the potential-function

$$ee'\frac{1}{r}+mm'\frac{a}{r^2},$$

and a might be referred to as the "size" of the ion.

§ Roughly, 700 in the hydrogen atom, and for other elements in proportion to the atomic weights of the elements. We here suppose the mass of the atom to consist solely of the masses of ions of which it is composed. See J. J. Thomson, Phil. Mag. vol. xlviii. p. 547, and earlier papers.

sisting of a large number of ions, is obviously impracticable. It is, however, known that the number of ions in an atom is very large, so that we shall attack the problem in the simple case of an "ideal" atom in which the ions are supposed to be so small that the number in an atom may be regarded as infinite. After the investigation it will be shown how it is possible to obtain an approximate knowledge of the spectrum of an atom which consists of a number of ions which is very great but is not infinite.

The ideal atom is to consist of a continuous distribution of electricity of density ρ. The corresponding density of matter is to be σ, so that it will ultimately be necessary to put $\sigma/\rho = \pm m/e$, where m/e is the ratio of the mass to the charge, in the case of the negative ions of the cathode rays. For the present, however, ρ and σ will be regarded as capable of independent variation. To correspond with the condition of spherical symmetry for the actual atom, it will be assumed that the distribution is arranged in spherical symmetry about some centre, so that both ρ and σ will be functions of the single coordinate r, the distance from the centre.

When the atom is at rest, every element is supposed to act on every other element with a force which acts along the line joining the two elements. The mutual potential of two elements at distance r and of volumes $dv\, dv'$ will be supposed to be

$$\{\rho\rho'\chi_1(r) + \sigma\sigma'\chi_2(r)\} dv\, dv',$$

and for large values of r this must reduce to $\rho\rho' r^{-1} dv\, dv'$.

When the atom is executing a small vibration, the forces may be supposed to be the same as if the atom were at rest in the displaced configuration. For in the case of a vibration of infinitesimal amplitude, the electromagnetic forces will vanish in comparison with the electrostatic, and it is easily verified that the velocity of propagation may, without appreciable error, be treated as infinite *.

§ 13. Let the whole atom undergo a small continuous displacement, so that the element of which the spherical polar coordinates before displacement were r, θ, ϕ is moved to $r+u$, $\theta+v$, $\phi+w$. In rectangular coordinates, which it will

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* Larmor, Camb. Phil. Trans. xviii. p. 391.

be convenient to use in conjunction with polars, let the element initially at x, y, z be displaced to $x+\xi$, $y+\eta$, $z+\zeta$.

Consider, in the first place, the field of force arising from the term $\chi_1(r)$ in the potential-function. The displacement of the element $\rho'\,dx'\,dy'\,dz'$ is equivalent to the creation of a doublet of moment

$$(\xi'\rho'\,dx'\,dy'\,dz',\ \eta'\rho'\,dx'\,dy'\,dz',\ \zeta'\rho'\,dx'\,dy'\,dz').$$

Hence the potential per unit charge, upon the element originally at x, y, z, but now at $x+\xi$, $y+\eta$, $z+\zeta$, which arises from the displacement of the foregoing element, will be

$$\rho'\,dx'\,dy'\,dz'\left\{(\xi'-\xi)\frac{\partial}{\partial x'}+(\eta'-\eta)\frac{\partial}{\partial y'}+(\zeta'-\zeta)\frac{\partial}{\partial z'}\right\}\chi_1(\mathrm{R})$$

where $\mathrm{R}^2=(x-x')^2+(y-y')^2+(z-z')^2.$

The potential arising from the displacement of the whole atom will therefore be

$$\mathrm{E}=\iiint\left\{(\xi'-\xi)\frac{\partial}{\partial x'}+(\eta'-\eta)\frac{\partial}{\partial y'}+(\zeta'-\zeta)\frac{\partial}{\partial z'}\right\}\chi_1(\mathrm{R})\rho'\,dx'\,dy'\,dz'.$$

The integration extends over the whole atom, but it will be convenient to take the integration throughout all space, writing $\rho=0$ at points outside the atom.

This potential may be at once transformed, so that we obtain

$$\mathrm{E}=-\iiint\left\{\frac{\partial}{\partial x'}(\xi'\rho')+\frac{\partial}{\partial y'}(\eta'\rho')+\frac{\partial}{\partial z'}(\zeta'\rho')\right\}\chi_1(\mathrm{R})\,dx'\,dy'\,dz'$$
$$+\left(\xi\frac{\partial}{\partial x}+\eta\frac{\partial}{\partial y}+\zeta\frac{\partial}{\partial z}\right)\iiint\chi_1(\mathrm{R})\rho'\,dx'\,dy'\,dz'.$$

Returning to polar coordinates, we can write $\mathrm{E}=\mathrm{E}_1+\mathrm{E}_2$, where

$$\mathrm{E}_1=-\iiint\left\{\frac{\partial}{r'^2\partial r'}(r'^2u'\rho')+\frac{\partial}{\sin\theta'\partial\theta'}(v'\rho'\sin\theta')+\frac{\partial}{\partial\phi'}(w'\rho')\right\}\chi_1(\mathrm{R})\,r'^2\sin\theta'\,dr'\,d\theta'\,d\phi'.$$

$$\mathrm{E}_2=\left(u\frac{\partial}{\partial r}+v\frac{\partial}{\partial\theta}+w\frac{\partial}{\partial\phi}\right)\iiint\chi_1(\mathrm{R})\rho' r'^2\sin\theta'\,dr'\,d\theta'\,d\phi'.$$

For any displacement which is continuous at the poles, $v/\sin\theta$ must be finite at both poles, and we may therefore assume expansions in the form

$$u=\Sigma\Sigma\alpha_n^m \mathrm{P}_n^m(\mu)e^{im\phi}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(v\sin\theta)=\Sigma\Sigma\beta_n^m\,\mathrm{P}_n^m(\mu)e^{im\phi},$$

$$w=\Sigma\Sigma\gamma_n^m\,\mathrm{P}_n^m(\mu)\,e^{im\phi} \quad . \quad . \quad . \quad . \quad (1)$$

where μ, as usual, stands for $\cos\theta$; n has all values from 0 to ∞, and m from $-n$ to $+n$, $\mathrm{P}_n^{-m}(\mu)$ being taken equal to $\mathrm{P}_n^m(\mu)$. The symbols α_n^m, β_n^m, γ_n^m, denote functions of r, and the letter m is not an index but is written from analogy with $\mathrm{P}_n^m(\mu)$. The expressions on the r.h. sides of (1) are capable of representing the most general displacements which are physically possible.

Substituting these values, E_1 can be written in the form

$$\mathrm{E}_1=-\Sigma\Sigma\iiint\left\{\frac{\partial}{r'^2\partial r'}(r'^2\alpha_n'^m\rho')+\rho'(\beta_n'^m+im\gamma_n'^m)\right\}\chi(\mathrm{R})$$
$$\mathrm{P}_n^m(\mu')e^{im\phi'}r'^2\sin\theta'\,dr'\,d\theta'\,d\phi'.$$

If we write γ for the angle between the radii r and r', so that

$$\cos\gamma=\cos\theta\cos\theta'+\sin\theta\sin\theta'\cos(\phi-\phi'),$$

we may expand $\chi_1(\mathrm{R})$ in the form

$$\chi_1(\mathrm{R})=\sum_0^\infty\tau_n\mathrm{P}_n(\cos\gamma),$$

where τ_n is a function of r, r' and of the coefficients which occur in $\chi_1(\mathrm{R})$. When R is so great that $\chi_1(\mathrm{R})$ becomes the same as R^{-1}, we have

$$\tau_n=r^n/r'^{n+1} \text{ or } r'^n/r^{n+1}, \text{ according as } r< \text{ or } >r'. \quad . \quad (2)$$

We can further expand the biaxal harmonic $\mathrm{P}_n(\cos\gamma)$ in the usual form, and so obtain

$$\chi_1(\mathrm{R})=\sum_{n=0}^{n=\infty}\sum_{m=0}^{m=n}\mathrm{C}_n^m\tau_n\mathrm{P}_n^m(\mu)\mathrm{P}_n^m(\mu')\cos m(\phi-\phi'),$$

where $\mathrm{C}_n^m=2\underline{|n-m}/\underline{|n+m}$ or 1, according as m is different from or equal to zero.

If we substitute this value for $\chi_1(\mathrm{R})$ in E_1, it appears that every term will vanish upon integration, except products of pairs of terms which are such that n and m are numerically the same for each. Performing the remaining integrations, we obtain

$$E_1 = \Sigma\Sigma\, F_n^m P_n^m(\mu) e^{im\phi}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where

$$F_n^m = -\frac{4\pi}{2n+1}\int\left\{\frac{\partial}{\partial r'}(r'^2 \alpha'^m_n \rho') + r'^2 \rho' (\beta'^m_n + im\gamma'^m_n)\right\}\tau_n dr'. \qquad (4)$$

The integral occurring in E_2 is that part of the potential of the whole atom upon a unit charge at the point r, θ, ϕ, which arises from the term $\chi_1(r)$ in the potential-function. This is obviously a function of r only; so that if we denote it by V_1, we have

$$E_2 = u\frac{\partial V_1}{\partial r}.$$

The remaining part of the potential-function may be treated in a similar way. If we expand $\chi_2(R)$ in the form

$$\chi_2(R) = \sum_0^\infty \lambda_n P_n(\cos\gamma),$$

we find for the potential of the whole displacement upon a unit mass initially at r, θ, ϕ the value $E_3 + E_4$, where

$$E_3 = \Sigma\Sigma\, G_n^m P_n^m(\mu) e^{im\phi},$$

where

$$G_n^m = -\frac{4\pi}{2n+1}\int\left\{\frac{\partial}{\partial r'}(r'^2 \alpha'^m_n \sigma') + r'^2 \sigma' (\beta'^m_n + im\gamma'^m_n)\right\}\lambda_n dr',$$

and

$$E_4 = u\frac{\partial V_2}{\partial r},$$

where V_2 is that part of the potential of the whole atom upon a unit mass at r, θ, ϕ which arises from the term $\chi_2(r)$ in the potential-function.

§ 14. The potential of the whole displacement upon the element initially occupying the volume $dx\,dy\,dz$ at x, y, z has been seen to be

$$\{\rho(E_1 + E_2) + \sigma(E_3 + E_4)\}\,dx\,dy\,dz.$$

Since the distribution of doublets which gives rise to the displacement-potential at x, y, z is of zero strength at x, y, z, the forces arising from the displacement can be calculated by differentiation. The differential operators must, however, act only upon those parts of the displacement-potential which are directly derived from $\chi_1(R)$ and $\chi_2(R)$, so that the term u which occurs in E_2 and E_4 will be exempt from differentiation.

If, for the sake of generality, we admit externally applied forces of amounts L, M, N per unit charge in the directions of r, θ, ϕ increasing, the equations of motion of the element initially at r, θ, ϕ will be

$$\sigma\frac{d^2u}{dt^2} = -\Sigma\Sigma\, P_n^m(\mu)e^{im\phi}\left(\rho\frac{dF_n^m}{dr} + \sigma\frac{dG_n^m}{dr}\right)$$

$$-u\left(\rho\frac{d^2V_1}{dr^2} + \sigma\frac{d^2V_2}{dr^2}\right) + L\rho, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\sigma\frac{d^2v}{dt^2} = -\Sigma\Sigma\frac{dP_n^m(\mu)}{rd\theta}\, e^{im\phi}(\rho F_n^m + \sigma G_n^m) + M\rho, \quad . \quad . \quad (6)$$

$$\sigma r\sin\theta\frac{d^2w}{dt^2} = -\Sigma\Sigma\frac{imP_n^m(\mu)}{r\sin\theta}\, e^{im\phi}(\rho F_n^m + \sigma G_n^m) + N\rho. \quad . \quad . \quad (7)$$

The Equations of Free Vibrations.

§ 15. Let us suppose that there is a normal vibration such that the element of which the equilibrium position is at r, θ, ϕ is found at time t at the point

$$r + ue^{ipt}, \quad \theta + ve^{ipt}, \quad \phi + we^{ipt},$$

u, v, w being given by scheme (1).

We write $L = M = N = 0$ in equations (5), (6) and (7); replace d^2/dt^2 by $-p^2$, and substitute for u, v, w from scheme (1). The resulting equations must then be identities for all values of r, θ, and ϕ.

To save printing, we shall write

$$W = \rho\frac{d^2V_1}{dr^2} + \sigma\frac{d^2V_2}{dr^2},$$

$$J_n^m = \rho F_n^m + \sigma G_n^m,$$

and

$$\frac{\delta J_n^m}{\delta r} = \rho\frac{dF_n^m}{dr} + \sigma\frac{dG_n^m}{dr}.$$

In this abbreviated notation, the transformed equations (5),

(6) and (7) are found to be

$$\sigma p^2 \Sigma\Sigma\, \alpha_n^m \mathrm{P}_n^m(\mu) e^{im\phi} = \Sigma\Sigma \left(\frac{\delta \mathrm{J}_n^m}{\delta r} + \alpha_n^m \mathrm{W} \right) \mathrm{P}_n^m(\mu) e^{im\phi}, \quad . \quad . \quad (8)$$

$$\sigma p^2 r^2 \Sigma\Sigma\, \beta_n^m \mathrm{P}_n^m(\mu) e^{im\phi} = \Sigma\Sigma\, \mathrm{J}_n^m \frac{1}{\sin\theta} \frac{d}{d\theta} \left\{ \sin\theta \frac{d\mathrm{P}_n^m(\mu)}{d\theta} \right\} e^{im\phi}, (9)$$

$$\sigma p^2 r^2 \sin^2\theta\, \Sigma\Sigma\, \gamma_n^m \mathrm{P}_n^m(\mu) e^{im\phi} = \Sigma\Sigma\, \mathrm{J}_n^m im \mathrm{P}_n^m(\mu) e^{im\phi}. \quad . \quad . \quad (10)$$

Equation (8) is expanded on both sides in zonal, tesseral, and sectorial harmonics, and is true for all values of θ and ϕ. We may therefore equate the coefficients of the various harmonics, and obtain

$$\sigma p^2 \alpha_n^m = \frac{\delta \mathrm{J}_n}{\delta r} + \alpha_n^m \mathrm{W}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In equations (9) and (10) we may begin by equating the coefficients of $e^{im\phi}$; multiply the equation obtained in this manner from (10) by $im/\sin^2\theta$ and add the result to the equation obtained by equating coefficients of $e^{im\phi}$ in (9). The result is

$$\begin{aligned} &\sigma p^2 r^2 \Sigma (\beta_n^m + im\gamma_n^m) \mathrm{P}_n^m(\mu) \\ &= \Sigma\, \mathrm{J}_n^m \left\{ \frac{1}{\sin\theta} \frac{d}{d\theta} \left\{ \sin\theta \frac{d\mathrm{P}_n^m(\mu)}{d\theta} \right\} - \frac{m^2 \mathrm{P}_n^m(\mu)}{\sin^2\theta} \right\}. \quad . \, (12) \end{aligned}$$

The right-hand member is equal to

$$-\Sigma n(n+1) \mathrm{J}_n^m \mathrm{P}_n^m(\mu),$$

and we are now able to equate coefficients of $\mathrm{P}_n^m(\mu)$. The equation so obtained, and equation (11), may be written

$$(\sigma p^2 - \mathrm{W}) \alpha_n^m = \rho \frac{d\mathrm{F}_n^m}{dr} + \sigma \frac{d\mathrm{G}_n^m}{dr}, \quad . \quad . \quad . \quad . \quad (13)$$

$$\sigma p^2 r^2 (\beta_n^m + im\gamma_n^m) = -n(n+1)(\rho \mathrm{F}_n^m + \sigma \mathrm{G}_n^m), \quad . \, (14)$$

while we have (*cf.* equation (4), p. 765)

$$\mathrm{F}_n^m = -\frac{4\pi}{2n+1} \int \left\{ \frac{d}{dr'} (r'^2 \rho' \alpha'^m_n) + r'^2 \rho' (\beta'^m_n + im\gamma'^m_n) \right\} \tau_n dr', \quad . \quad (15)$$

$$\mathrm{G}_n^m = -\frac{4\pi}{2n+1} \int \left\{ \frac{d}{dr'} (r'^2 \sigma' \alpha'^m_n) + r'^2 \sigma' (\beta'^m_n + im\gamma'^m_n) \right\} \lambda_n dr'. \quad (16)$$

Equations (13) to (16) must hold for all values of r, and contain only the four variables α_n^m, $\beta_n^m + im\gamma_n^m$, F_n^m, and G_n^m, each equation being homogeneous and of the first degree in these four variables. It is easily seen that there is no solution of these equations other than

$$\alpha_n^m = 0, \quad \beta_n^m + im\gamma_n^m = 0, \quad F_n^m = 0, \quad G_n^m = 0, \quad . \quad . \quad (17)$$

except only when a special relation is satisfied by the various constants of the equations. Now m has entirely disappeared, so that any such relation may be written in the form

$$f(p^2, n) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where the coefficients which determine the functional form f are constants of the atom and of the potential-function.

Hence the normal vibrations fall into two classes, given by the two equations (17) and (18) respectively. In either class the displacement exists only for single values of n and m.

For a vibration of the first class $\alpha_n^m = 0$, and β_n^m, γ_n^m may have any values such that

$$\beta_n^m + im\gamma_n^m = 0.$$

The displacement is purely tangential, and no forces of restitution are called into play. Hence the frequency is in every case $p = 0$ (as is otherwise obvious from equations (9) and (10)), and, strictly speaking, the corresponding normal degrees of freedom do not give rise to vibrations at all.

For a vibration of the second class, the frequency is a root of equation (18), and the functions α_n^m, $\beta_n^m + im\gamma_n^m$, F_n^m, G_n^m are determined by equations (13) to (16). These functions do not contain m; to determine β_n^m and γ_n^m separately we must give to m any one of the $(2n+1)$ integral values between n and $-n$, and determine β_n^m, γ_n^m from equations (9) and (10), in this way obtaining $(2n+1)$ independent normal vibrations. the frequency of each being the same.

From the manner in which the analysis has been conducted, it will be clear that all possible normal vibrations must have been taken into account.

The Spectrum of the Ideal Atom.

§ 16. For the vibrations of the first class $p = 0$; so that these vibrations are not represented in the visible spectrum.

The frequencies of the second class of vibration are all contained in equation (18). Solving for p^2, this equation can be split up into the separate equations

$$p^2=f_1(n),$$
$$p^2=f_2(n), \quad \&c.$$

Any one of these equations gives rise to a simply infinite series of lines in the spectrum, the wave-lengths of the lines in any such series being found by assigning the various positive integral values to n, in a formula in which n alone varies. Such a collection of lines will be referred to as a "spectrum-series." It has accordingly been shown that the visible spectrum of the ideal atom can be sorted out into a collection of spectrum-series; and it has also been shown that the nth line in each series must be regarded as the superposition of of $(2n+1)$ equal free periods.

Heads of Spectrum-Series.

§ 17. It can be shown that every spectrum-series tends to a definite limit corresponding to $n=\infty$, and the position of the line $n=\infty$ will accordingly be referred to as the "head" of the series.

The heads of the various series will be given by (*cf.* equation 18)

$$f(p^2, \infty)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

this equation being the result of eliminating the four variables from equations (13) to (16) after putting $n=\infty$.

Let us begin with the consideration of the form assumed by equation (15) when $n=\infty$. We have

$$\chi_1(\mathrm{R})=\sum_0^\infty \tau_n \mathrm{P}_n(\cos\gamma),$$

where

$$\frac{1}{\mathrm{R}}=\frac{1}{\sqrt{r^2-2rr'\cos\gamma+r'^2}}=\sum_0^\infty \frac{r^n}{r'^{n+1}}\mathrm{P}_n(\cos\gamma),$$

in the case in which $r'>r$. Since $\chi_1(\mathrm{R})$ becomes identical with R^{-1} except for small values of r, we may assume

$$\tau_n=\frac{r^n}{r'^{n+1}}(1+\delta_1),$$

when $r' > r$, where δ_1 is a series in descending powers of r' and ascending powers of r, which is very small except near to the value $r' = r$. Similarly we may assume

$$\tau_n = \frac{r'^n}{r^{n+1}}(1+\epsilon_1),$$

when $r' < r$, where ϵ_1 is a similar series in ascending powers of r' and descending powers of r. At $r = r'$, $(1+\delta_1)$ and $(1+\epsilon_1)$ must have a common limit $(1+\zeta_1)$.

In the identities

$$\int_0^r f_1(r') \frac{r'^n}{r^{n+1}} dr' = \frac{f_1(r)}{n+1} - \frac{1}{n+1}\int_0^r r' \frac{\partial f_1(r')}{\partial r'} \frac{r'^n}{r^{n+1}} dr',$$

$$\int_r^\infty f_2(r') \frac{r^n}{r'^{n+1}} dr' = \frac{f_2(r)}{n} + \frac{1}{n}\int_r^\infty r' \frac{\partial f_1(r')}{\partial r'} \frac{r^n}{r'^{n+1}} dr',$$

put $f_1(r') = \phi(r')(1+\delta_1)$, $f_2(r') = \phi(r')(1+\epsilon_1)$ and add. We obtain

$$\int_0^\infty \phi(r')\tau_n dr' = \frac{2n+1}{n(n+1)}\phi(r)(1+\zeta)$$
$$+ \text{ terms of lower degree in } n.$$

The function λ_n may be treated in the same way as τ_n, except that the principal term r^n/r'^{n+1} or r'^n/r^{n+1} is wanting. We therefore assume

$$\lambda_n = \frac{r^n}{r'^{n+1}}\delta_2 \text{ between } r' = r \text{ and } \infty,$$

$$\lambda_n = \frac{r'^n}{r^{n+1}}\epsilon_2 \text{ between } r' = 0 \text{ and } r,$$

where δ_2, ϵ_2 are similar to δ_1 and ϵ_1, and have a common limit ζ_2 at $r = r'$.

Writing Y for α_n^m and Z for $\beta_n^m + im\gamma_n^m$, we are now able to expand equations (15) and (16) in the form

$$F_n^m = -\frac{4\pi\rho}{n(n+1)}\left\{\frac{d}{dr}(r^2\rho Y) + r^2\rho Z\right\}(1+\zeta_1)$$
$$+ \text{ terms of lower degree in } n, \quad . \quad . \quad . \quad (20)$$

$$G_n^m = -\frac{4\pi\sigma}{n(n+1)}\left\{\frac{d}{dr}(r^2\sigma Y) + r^2\sigma Z\right\}\zeta_2$$
$$+ \text{ terms of lower degree in } n. \quad . \quad . \quad . \quad (21)$$

Substituting these values for F_n^m and G_n^m in equations (13) and (14), and putting $n=\infty$, we find as the equivalent of equations (13) to (16) the two equations

$$(\sigma p^2-W)Y=0, \qquad (22)$$

$$\{\sigma p^2-4\pi\rho^2(1+\zeta_1)-4\pi\sigma^2\zeta_2\}Z=0. \qquad (23)$$

§ 18. These equations are not difficult to interpret. Corresponding to any value of n, the displacement-potential at r of the shell of radius r' contains the factor r^n/r'^{n+1} or $r'^n/^{n+1}$, according as $r<$ or $>r'$. This shows that in the case of $n=\infty$, the potential created by the displacement of any shell will vanish everywhere except in the immediate neighbourhood of that shell. It is therefore clear that the normal vibrations for which $n=\infty$ will split up into the normal vibrations of the separate shells.

This is the meaning of equations (22) and (23). Corresponding to a given value of p^2, the second factors of equations (19) or (20) can only vanish over a single isolated shell of ions; hence the first factor must vanish everywhere except over this shell. The corresponding displacement and displacement-potential are limited to the shell in question.

Corresponding to any specified shell, equations (22) and (23) show that there will be two vibrations of order $n=\infty$. For the first of these $Z=0$ and $\sigma p^2=W$. For the second, $Y=0$ and $\sigma p^2=4\pi\{\rho^2(1+\zeta_1)+\sigma^2(1+\zeta_2)\}$. The displacement of the shell is therefore in the former case purely radial; in the latter purely tangential.

§ 19. This concludes the investigation of the frequency-equation for the case of $n=\infty$. Corresponding to each particular solution for the case of $n=\infty$, there will be a general solution for all values of n from 0 to ∞. Hence the number of spectrum-series will be equal to twice the number of shells in the atom. The frequencies of the heads of the series are, as we have seen, given by

$$p^2=\frac{W}{\sigma}, \qquad (24)$$

$$p^2=\frac{4\pi}{\sigma}\{\rho^2(1+\zeta_1)+\sigma^2\zeta_2\}. \qquad (25)$$

§ 20. It is easily verified that all possible degrees of freedom have been accounted for. The $(2n+1)$ degrees represented by the nth line of a spectrum-series may be associated with the $(2n+1)$ independent spherical surface-harmonics of order n; so that a complete spectrum-series may be associated with the most general function of position on any spherical surface. Writing Δ for $\frac{1}{\sin\theta}\frac{d}{d\theta}(v\sin\theta)+\frac{dw}{d\phi}$, the tangential dilatation, we see that the two spectrum-series corresponding to any single shell may be associated with the most general distribution of u and Δ which is possible over the surface of the shell in question. Combining the series from all the shells, we find that we can now associate a free-period with every degree of freedom implied in the possibility of giving arbitrary values to u and Δ at every point of every shell. The remaining degrees of freedom can be accounted for by adding to the foregoing distribution of u and Δ a distribution of displacement for which $u=0$ and $\Delta=0$ everywhere. These are the tangential degrees of freedom of the first class, for which $p^2=0$.

Numerical Calculation of the Size of an Atom.

§ 21. From equation (25) we can form an estimate of the size of atom which would be required in order to give vibrations comparable in frequency with those of light.

As regards order of magnitude, we may take $p^2=10^{31}$ $\rho/\sigma=e/m=\pm 10^7$, $\rho^2(1+\zeta_1)+\sigma^2\zeta_2=\rho^2$; and these values substituted in (25) give $\rho=10^{23}$, as regards order of magnitude. The charge on a single negative ion is 6×10^{-10}, so that the number of ions per cub. centim. is of the order of 2×10^{32}. In an atom of atomic weight n, the number of ions is of the order of $10^3 n$, so that the radius of the atom will be $n^{\frac{1}{3}}10^{-9}$ cm.

The Spectrum of a Real Atom.

§ 22. It will be convenient at this stage to examine to what extent it is possible to deduce the spectrum of a real atom (as we are imagining it to be) from the spectrum of the ideal atom which has so far been the subject of investigation.

Let us consider a real atom I consisting of a finite number of ions A, B, C . . . . . We are going to compare this with an ideal atom I′, consisting of a finite number of elements of volume A′, B′, C′ . . . . . These elements can always be chosen (since the whole structure of I′ is, up to the present, at our disposal) so that the total charge in the element A′ is all of the same sign, and equal to the charge of the ion A. In this case, since we shall suppose the ratio of the charge to the mass to be numerically equal to the same constant for both atoms, the mass of the element A′ will be equal to the mass of the ion A′.

The position of the element A′ is as yet undetermined; but the more closely the atom I approaches to spherical symmetry of structure the more nearly will it be possible to arrange the ideal atom in such a way that, if we imagine the two atoms "superposed" (made to occupy the same space), then the ion A will be near to the element A′, B to B′, and so on, while at the same time the ideal atom shall satisfy the condition of perfect spherical symmetry.

In order to avoid a discussion of continuity at points at which the electrical density changes sign, we may suppose elements for which ρ is of different sign to be separated by a thin transition-layer of thickness small in comparison with the dimensions of an element.

Imagine the ideal atom subjected successively to a system of displacements finite in number, say

$$u = r^s S_t, \quad \Delta = 0,$$

or

$$u = 0, \qquad \Delta = r^s S_t,$$

where Δ, as in § 20, denotes the tangential dilatation, S_t denotes a surface harmonic of order t, and s, t have any number of integral values. For each of these displacements calculate the forces acting upon each of the elements A′, B′, ... ; these will be linear functions of C_1, C_2, ... , the constants which may be supposed to enter in the specification of the law of force in the ideal atom. In order that the forces calculated in this way may be finite, it is necessary and sufficient that the forces between elements at a small distance r shall be of an order not greater than $\frac{1}{r^2}$ in $\left(\frac{1}{r}\right)$.

Imagine the real atom to undergo the same system of displacements, and for each of these displacements calculate the forces acting upon each of the ions in terms of the constants which occur in the actual law of force between ions (supposed known). Now equate the forces acting upon A to the forces acting upon A′ in the case of the same displacement. We see in this way that the forces acting on A, B, C . . . . can be made identical with the forces acting on A′, B′, C′ . . . . for the case of any finite number of displacements (the number being as large as we please so long as it is not infinite) provided that the infinite number of constants C_1, C_2 . . . . satisfy a finite number of linear algebraical equations.

Corresponding to any selected system of displacements it will be possible to find C_1, C_2 . . . ., so that the forces acting upon corresponding elements and ions may be equal in every case. Cases of failure (cases in which two or more of the equations for C are inconsistent with finite values for C) can always be avoided by slightly altering one or more of the selected displacements. If the displacements are suitably chosen, it will be possible very approximately to expand any normal displacement of the ideal atom as a sum of these displacements. Hence the forces acting upon any element A′ of the ideal atom when this atom undergoes any one of its normal displacements will be very approximately equal to the forces acting upon the ion A when the real atom undergoes the same displacement.

But the ion A is very nearly in the position corresponding to that occupied by the element A′, and the total mass of the element A′ is equal to the mass of the ion A. Hence the integral mass-displacement of the element A′ is very nearly equal to the mass-displacement of the ion A.

It follows that the free vibrations of the ideal atom I′ will be very approximately reproduced, as regards both frequency and displacement, in the real atom I, provided only that we select the imaginary law of force for the ideal atom in the manner indicated above. It is easy to see that this imaginary law of force must approximate at infinite distances to the limit of the real law at infinite distances, namely the ordinary electrostatic law. Hence, so long as we make no assumptions about this imaginary law except that at infinite distances it approximates to the ordinary electrostatic law (the assumption which was made in §§ 12, 17), we shall be justified in supposing that every quantitative result obtained for the free vibrations of the ideal atom will be very approximately a reproduction of a similar result for the real atom.

§ 23. It follows that there must be a line of the real spectrum in the neighbourhood of every line of the ideal spectrum. Confining our attention to the lines of a single spectrum-series of the ideal spectrum, we see that the lines must be approximately reproduced, line for line, in the real spectrum, until we reach such large values of n that the distance between successive lines becomes comparable with the error of our approximation : after this it will be impossible to trace corresponding lines. This last result is, from another point of view, obvious : when the order n of an harmonic becomes comparable with the number of ions on a great circle of an atom, it is impossible to distinguish a displacement of the real atom given by an harmonic of order n from one given by an harmonic of different order.

§ 24. For one kind of spectrum-series which occurs in the ideal spectrum (equation (25), p. 771), the value of p^2 at the head is equal to $(\rho^2(1+\zeta_1)+\sigma^2\zeta_2)/\sigma$. When the transition-layers are supposed to be infinitely thin, this may be regarded as a continuous function of r. Hence the heads of these series will form a continuous band of light.

This, however, is not true for lines of the spectrum-series other than the head, since it is only for $n=\infty$ that ρ enters the frequency equation through its square, and expressions which contain odd powers of ρ must not be regarded as continuous functions of r. Hence the lines in the spectrum-series corresponding to values of n other than $n=\infty$, cannot be regarded as forming continuous bands of light*.

It will be seen that such a group of lines may be regarded as forming two striated bands of light. A line will fall into one band or the other according to the sign of ρ for the shell with which it is associated, the dark places in one band corresponding to the bright places in the other.

In the case of the real atom, this will give two separate groups of spectrum-series. Each group will consist of a number of adjacent spectrum-series, and the two groups will have (approximately) a common head. The various series correspond to the various shells of ions in the atom; those in one group correspond to shells of negative ions, those in the other to shells of positive ions. We may imagine the vibrations associated with the innermost shells of ions to be of less energy than those associated with the outer shells, and in this case the lines of a given order (n) in either group will themselves form a series of lines of diminishing brightness, until the lines become so faint as to be invisible.

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* Otherwise thus :—The continuity in the ideal spectrum, in the case of every value of n except $n=\infty$, is effected by the vibrations associated with the thin transition-layers, and these have no actual existence.

The spectrum-series of the real atom which correspond to the ideal spectrum-series of which the heads are given by equation (24) will similarly fall into two groups, but the series of any groups will be adjacent only if W varies continuously from ion to ion as we pass inwards from the surface of the atom.

§ 25. It will be at once seen that the arrangement of spectrum-series just found is sufficiently general to describe the arrangement which is known to exist in an actual atom. The adjacent series forming a single group may be supposed to form the series of triplets, double or single lines which occur in observed spectra. The two classes of series corresponding to equations (24) and (25) will be the principal and subordinate (or else subordinate and principal) series of the classification of Kayser and Runge. The two sets of subordinate series (the first and second according to Kayser and Runge; the 'nébuleux' and 'étroit' according to Rydberg) will be the two groups of one of the two classes given by (either) equation (24) or (25). It does not seem possible to identify the various series of our theory with observed series without carrying our theory much further than has been done at present. But enough has, perhaps, been said to show that the general arrangement of lines in the spectrum which is predicted by our theory is sufficiently general to include that which is observed, while being at the same time sufficiently definite to afford a test of capability of the atom as we are now imagining it to reproduce the phenomena of the natural atom.

§ 26. A comparison between the theoretical and observed spectrum suggests that the actual atom may be regarded as approximately made up of shells of ions of alternate signs, or, still better, of shells of doublets. The same conclusion might have been arrived at from a consideration of the conditions of either equilibrium or stability. The evidence of the Zeeman phenomenon—that the predominating vibrations are those of negative ions, as well as the experimental result that negative ions are dissociated from the atom more readily than positive ions (there being no evidence that these latter can be dissociated at all), leads to the conclusion that the outermost layer of ions is of negative sign.

§ 27. The class of tangential vibrations of frequency $p^2=0$ which was found for the ideal atom (§ 15) will be approximately reproduced in the real atom. The corresponding values of p^2 will not now be actually zero, but will be very small.

Hence, in addition to the spectrum already discussed, which has been shown to consist solely of a collection of spectrum-series, there will be a second spectrum, far removed from the former, and at the infra-red end of it. It is not practicable to investigate the positions or arrangement of the lines of this spectrum, since the whole value of p^2 consists of a correction arising from the discrete structure of the atom. At the same time the existence of this spectrum might throw some light on the phenomenon of "electromagnetic resonance" discovered by Drude. It is found that resonance can be established between matter (in the case of certain substances at least) and electromagnetic waves of which the frequency is only about a millionth part of the frequencies of the visible spectrum*.

The Zeeman Phenomenon.

§ 28. Let us return to the general equations of the ideal atom, found in § 14, and suppose that u, v, w specify a normal vibration under the influence of a magnetic field H, parallel to the axis of the molecule. We must in this case write

$$L = \mathrm{H}ip\,r\,w\sin^2\theta,$$

$$M = \mathrm{H}ip\,r\,w\sin\theta\cos\theta,$$

$$N = -\mathrm{H}ip\,(rv\cos\theta + u\sin\theta).$$

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* Wied. *Ann.* lviii. p. 1; lix. p. 17; lxiv. p. 131.

Writing E for $\rho \mathrm{E}_1 + \sigma \mathrm{E}_3$ (§ 13) and

$\delta \mathrm{E}/\delta r$ for $\rho d\mathrm{E}_1/dr + \sigma d\mathrm{E}_3/dr$,

the equations of motion will be (*cf.* equations 8, 9, 10, p. 767)

$$\sigma p^2 u = \frac{\delta \mathrm{E}}{\delta r} + u\mathrm{W} - \rho \mathrm{H} ip\, r\, w \sin^2\theta, \quad . \quad . \quad . \qquad (26)$$

$$\sigma p^2 r^2 v = \frac{d\mathrm{E}}{d\theta} - \rho \mathrm{H} ip\, r^2\, w \sin\theta \cos\theta, \quad . \quad . \quad . \qquad (27)$$

$$\sigma p^2 r^2 \sin^2\theta w = \frac{d\mathrm{E}}{d\phi} + \rho \mathrm{H} ip\, r \sin\theta (rv \cos\theta + u \sin\theta). \quad . \qquad (28)$$

We shall only attempt the solution upon the supposition that H^2 may be neglected, and in this case we obtain from (26) and (28)

$$\sigma p^2 u = \frac{\delta \mathrm{E}}{\delta r} + u\mathrm{W} - \frac{\rho \mathrm{H} ip}{\sigma p^2 r} \frac{d\mathrm{E}}{d\phi}.$$

Equating the various harmonics in this, we obtain (*cf.* equation 11, p. 767)

$$\sigma p^2 \alpha^m_n = \frac{\delta \mathrm{J}^m_n}{\delta r} + \alpha^m_n \mathrm{W} + \frac{\rho \mathrm{H} m}{\sigma p r} \mathrm{J}^m_n. \quad . \quad . \quad . \qquad (29)$$

Similarly we obtain from (27) and (28),

$$\sigma p^2 r^2 v = \frac{d\mathrm{E}}{d\theta} - \frac{\rho \mathrm{H} ip}{\sigma p^2} \cot\theta \frac{d\mathrm{E}}{d\phi}.$$

Equating coefficients of $e^{im\phi}$, multiplying by $\sin\theta$, and operating with $\dfrac{1}{\sin\theta}\dfrac{d}{d\theta}$, we get

$$\sigma p^2 r^2 \Sigma \beta^m_n \mathrm{P}^m_n(\mu) = \left\{ \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\mathrm{P}^m_n(\mu)}{d\theta} \right) \right.$$
$$\left. + \frac{\rho \mathrm{H} m}{\sigma p \sin\theta} \frac{d}{d\theta} (\cos\theta \,.\, \mathrm{P}^m_n(\mu)) \right\} \mathrm{J}^m_n. \quad . \qquad (30)$$

From (28), with the help of (26) and (27),

$$\sigma p^2 r^2 \sin^2\theta w = \frac{d\mathrm{E}}{d\phi} + \frac{\rho \mathrm{H} ip}{\sigma p^2} \left(\sin\theta \cos\theta \frac{d\mathrm{E}}{d\theta} + r \sin^2\theta \frac{\delta \mathrm{E}}{\delta r} \right).$$

Equate coefficients of $e^{im\phi}$, multiply by $im/\sin^2\theta$, add to

(30) and we obtain, after some simplification,

$$\sigma p^2 r^2 \Sigma(\beta_n^m + im\gamma_n^m)\mathrm{P}_n^m(\mu)$$
$$= -\Sigma\left(n(n+1) + \frac{\rho \mathrm{H} m}{\sigma p}\right)\mathrm{P}_n^m(\mu)\mathrm{J}_n^m$$
$$- \frac{\rho \mathrm{H} m}{\sigma p}\Sigma r \frac{\delta \mathrm{J}_n^m}{\delta r}\mathrm{P}_n^m(\mu).$$

We can now equate coefficients and obtain

$$-\sigma p^2 r^2(\beta_n^m + im\gamma_n^m) = \left\{n(n+1) + \frac{\rho \mathrm{H} m}{\sigma p}\right\}\mathrm{J}_n^m + \frac{\rho \mathrm{H} m r}{\sigma p}\frac{\delta \mathrm{J}_n^m}{\delta r}. \quad (31)$$

It appears, therefore, that under the influence of a magnetic field, the normal coordinates will fall into the same two classes as before. The frequency of the lines of the visible spectrum is, however, no longer given by equation (18) but by an equation of the form

$$f(p^2, n) + \mathrm{H}pm\mathrm{F}(p^2, n) = 0. \quad . \quad . \quad . \quad . \quad (32)$$

§ 29. We see from this that the effect of the magnetic field is to separate the $(2n+1)$ lines, which, in the absence of a magnetic field, coincide in the nth line of a spectrum-series, in such a way that the line $m=0$ remains in its original position and forms the central one of a group of $(2n+1)$ equidistant lines. Thus the line $n=0$ will be unaffected by a magnetic field, the line $n=1$ separated into a symmetrical triplet, the line $n=2$ into an evenly-spaced quintet, and so on.

§ 30. The lines of the spectrum of the actual atom must be influenced by a magnetic field in a manner approximately the same as that found for the ideal atom. It may, however, happen that some of the side lines will be too faint for observation. It may also happen that the $(2n+1)$ lines did not originally form a single coincident line, but a doublet or even more complex structure. It may thus happen that the number of equal periods represented by any single line is an even number. In this case it is known that the lines must spread symmetrically * so that there will be no middle line left, and the separated line will consist of a doublet, quartet, &c.

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* Lorentz, Astrophys. Journal, ix. p. 37.

The solution of equation (32) will be of the form

$$p = \phi(n) + \mathrm{H}m\Phi(n),$$

where ϕ and Φ are the same for the same spectrum-series.

The separation is therefore directly proportional to the strength of the field; and we can see reasons for expecting the remaining factor to be intimately dependent upon the spectrum-series to which the line belongs, as well as upon its position in this series.

§ 31. In considering the polarization of the various lines, we shall neglect the ratio of the radius of the atom to the wave-length. In this case the radiation emitted by the atom may be taken to be the same as the radiation emitted by an "equivalent particle," this particle moving so that its displacement multiplied by its charge is equal to the vector-sum of the displacements of the ions of the atom multiplied by their various charges*.

We have seen that the central line of a Zeeman group is emitted by a vibration which is specified by a zonal harmonic, having the direction of magnetic force as axis. The orbits of the ions are therefore in the meridional planes, and are the same in all such planes. The resultant radiation is therefore such as would be emitted by a single particle vibrating along the axis.

The vibrations by which the side lines are emitted may each be regarded as composed of two parts :—

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* The radiation emitted by a vibrating system of ions can be calculated as follows:—Let the displacement arising from a single vibration be such that ξ, η, ζ (the components along three rectangular axes) are the real parts of αe^{ipt}, βe^{ipt}, γe^{ipt}, and introduce a complex vector $\mathbf{C}$ of which the components are α, β, γ. Then the radiation at an external point can be determined from the single vector $\mathbf{P}$ which is the real part of

$$e^{ipt}\iiint \mathrm{R}^{-1}e^{-ip\mathrm{R}/\mathrm{V}}\rho\mathbf{C}\,dx\,dy\,dz,$$

where R is the distance of the external point from the element $dx\,dy\,dz$. When we neglect the radius of the atom we may take $\mathrm{R}^{-1}e^{-ip\mathrm{R}/\mathrm{V}}$ outside the integral, and this leads to the rule for the vector composition of displacements. The radiation is given by the equations

$$\mathbf{E} = \frac{1}{\mathrm{V}^2}\frac{d^2\mathbf{P}}{dt^2}, \quad \mathbf{H} = -\frac{1}{\mathrm{V}}\frac{d}{dt}(\mathrm{curl}\ \mathbf{P}).$$

Cf. Larmor, Æther and Matter, §§ 151–156.

(α) A vibration parallel to the axis of harmonics.

(β) A vibration in which every ion describes an orbit parallel to the equatorial plane.

The amount of the former will be different in different meridional planes. Since this amount will, for the line m, contain the factor $e^{im\phi}$, we see that the aggregate radiation is *nil*.

The amount of the latter will also be proportional to a factor $e^{im\phi}$, and the radiation will be *nil* except in the case of $m = \pm 1$.

In the case of $m=1$, the radiation is such as would be emitted by a single particle describing an orbit in the equatorial plane. To investigate this orbit it is only necessary to notice that the values of u, v, w at every point will depend on ϕ and t only through the factor $e^{i(m\phi+pt)}$. Hence the equivalent displacement will depend on ϕ and t through the same factor, and will therefore be that of a particle describing a circle in the equatorial plane, the direction being that of ϕ increasing or decreasing according as m has the value -1 or $+1$.

Hence the polarization of the lines $m = -1, 0, +1$ can be accounted for in the manner in which they have already been accounted for by Larmor upon the supposition that the radiation is emitted by a single ion vibrating in a spherically symmetrical field of force. On the other hand, our theory does not compel us to expect that every line will be separated into a triplet, or that the separation will be of constant amount.

§ 32. It must be remembered that our examination of the polarization is subject to two corrections: one arising from the finite radius of the atom (which was neglected in comparison with the wave-length), and the other from the discrete structure of the actual atom. For this reason we cannot expect the polarization of the lines to be absolutely complete, and the lines for which m has values other than 0 or ± 1 will not actually be invisible, although since the total radiation arises solely from two small corrections, they will probably be very faint.

The polarization of the side-lines of a triplet shows that the equivalent single ion must be supposed to be of negative sign. It is of interest to notice that on the present theory this does not indicate that the light is emitted solely by negative ions, but only that the vibrations of the negative ions contribute more to the radiation of the particular periods in question than do the positive ions (see § 26).

The Influence of the Translation and Rotation of the Atom.

§ 33. There is a purely kinematical result of the translational motion of the atom, which shows itself in the well-known Doppler effect, and consequent broadening of the spectral lines. In addition to this, the actual periods of vibration of the atom are altered by its velocity in space. It has been shown by Lorentz that the effect of a uniform velocity of translation $(u, 0, 0)$ is to decrease the components along the axis of x of all the electrical forces involved, in the ratio $1 : (1-u^2/V^2)^{\frac{1}{2}}$, where u is the total velocity of the atom relatively to the æther.

The result of this is that the spherical symmetry of the atom is destroyed, and the lines in the spectrum which have been supposed to be superposed and indistinguishable will become separated. It is, however, easily verified that this separation will be much too small to be capable of observation.

The view which we have taken up compels us to suppose that the linear dimensions, not only of atoms, but of complete bodies, depends upon their orientation in space. It has been pointed out by Lorentz *, Larmor †, and Walker †, that this supplies the only satisfactory explanation of Michelson's aberration experiments.

§ 34. The influence of the rotation of the atoms will, like that of the translation, be two-fold. There is, first, a purely kinematical effect, already discussed in § 2, and, second, a dynamical effect, as follows:—

We can allow for a rotation w, by supposing a force $w^2 r \sin \theta$ to act per unit mass, perpendicular to the axes of the atom. The effect of this, regarded as a steady force, will be to produce a new equilibrium configuration, each element being moved a slight distance from its old position.

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* Lorentz, *Versuch einer theorie* . . . p. 120.

† Adams Prize Essays, 1900.

The vibrations will now be vibrations about this displaced position of equilibrium, under the influence, partly of the displacement-potential, and partly of the centrifugal force which is supposed to act.

The periodicities will therefore be slightly changed, and the amount of change for every vibration will contain w^2 as a factor.

Remembering that w^2 varies from atom to atom, it appears that the effect upon the spectrum of the whole gas, which is produced by allowing for the rotation of the atoms, will be to change each line into a band. The centre of the band will not coincide with the original line; the position of this line will now be occupied by the extreme edge of the band, corresponding to $w=0$, and since the probability of zero rotation is *nil* for each atom, this line will be of zero intensity.

We have, however, seen that each "line" of the original line-spectrum ought to be regarded as the superposition of several lines. The rotation of the atom destroys the spherical symmetry, and therefore separates these lines, each one being, at the same time, spread out into a band.

The resulting "band" will therefore be a more complex structure than we have hitherto supposed it to be. It may, for instance, spread to both sides of the original line, and may show several maxima and minima of intensity. But in every case the widening effect ought to remain always similar to itself, the amount being always proportional to $\bar{w}^2$, the mean value of w^2.

Now if the rotation is governed by a subsidiary temperature, $\bar{w}^2$ will be proportional to the temperature, and therefore to the density (§ 6), so that the shift and the broadening of any line will each be directly proportional to the pressure in a pure gas, and roughly proportional to the total pressure in a mixed gas*.

In any single spectrum-series, not only the periodicity but also the form of the normal function depends solely upon the single parameter n. From this it follows that the amount of shift in a single spectrum-series will depend only on n.

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* A Summary of Experimental Knowledge is given by W. J. Humphreys, Astrophys. Journal, vi. p. 225.

There will therefore be a similarity between the shift of the different lines of the same series, such as does not exist between those of different series.

The broadening effect just found must be added to that of § 8. The broadening due to each effect, and therefore also the resultant broadening, will be proportional to the pressure.

§ 35. In the case of complete molecules the rotation will not be governed by a subsidiary temperature, so that the effect of rotation will be much greater than in the case of dissociated atoms. There need therefore be no difficulty in accounting for the continuous spectrum emitted by a solid or a heated gas.

The Structure of Molecules.

§ 36. Let us now pass from the consideration of the phenomena of spectroscopy to the consideration of the other properties of matter which are implied in our provisional view of the structure of an atom.

If an atom consists of n negative and $n+s$ positive ions, the total charge on the atom will be se, and s may, by a slight extension of the usual terminology of chemistry, be referred to as the valency of the atom.

It is clear that there will be no atom of which the valency s is comparable with n, since such an atom would tend to expel the ions of that sign which was in the majority, although, when s is small compared with n, the corrections which we have seen must be applied to the ordinary electrostatic law may be sufficient to counterbalance this tendency.

An atom of valency s behaves at sufficient distances from its surface like an electrostatic point-charge of electricity se placed at its centre. We may therefore expect that under favourable conditions the atoms will combine into larger systems, namely molecules, a molecule being now defined as a system of ions of which the total charge is zero.

Thus an atom of valency -2 may combine with another atom of valency $+2$, or with two atoms each of valency $+1$, and so on. Or two similar atoms each of valency ± 1 may combine with two ions to form a neutral molecule, though, by hypothesis, a single such atom cannot combine in a stable manner with a single ion. So two atoms of valency ± 1

may combine and form a neutral body, by ejecting the two superfluous ions.

On this view, a molecule of an element cannot be the same as two (or more) atoms, although the molecule of a compound may or may not be a sum of atoms of elements. But it follows from the definition of a molecule, as a system of which the total charge is zero, that no free ions can be liberated by chemical change. It follows further that the force exerted by a complete molecule at external points will fall off very rapidly as we recede from the molecule.

Electrostatical Forces.—Chemical Affinity, Cohesion.

§ 37. We may examine the electrostatic field of force more closely as follows.

With core as origin of coordinates, the potential of an atom upon an ion exterior to it (and at a distance so great that the unknown part of the potential function may be ignored) can be written

$$V = \frac{a_0}{r} + \frac{S_1}{r^2} + \frac{S_2}{r^3} + \dots \quad . \quad . \quad . \quad . \quad (33)$$

where S_1, S_2, ... are spherical surface-harmonics of orders 1, 2, ...

Now

$$\iint \frac{dV}{dr} r^2 \, d\theta \sin\theta \, d\phi = 4\pi \times \text{total convergence of force inside atom,}$$

$$= -4\pi se.$$

Substituting for V the value given by equation (33), we find that a_0/r is the *chemical* force, a_0 being proportional to the valency of the atom.

Hence between two atoms there will be a chemical attraction or repulsion along the line joining their centres, and also a force (proportional to $1/r^3$ at most) arising from the coarse-grainedness of the ionic structure. Between two molecules the latter force exists alone.

This latter force (force of cohesion) will be vanishingly small in a gas, where the distance between adjacent molecules is small compared with scale of coarse-grainedness of atoms, but may become very large in a solid.

The force consists of a couple and a radial force. From the form of V these are equally likely, if the atoms are placed at random, to be in either direction. But if the atoms (or molecules) are permanently near one another, the couple will turn them into a position in which this potential is a minimum (and therefore, speaking roughly, negative), and the radial force dV/dr is now attractive.

Electrodynamical Forces.—Permanent and Induced Magnetism.

§ 38. In addition to the forces just considered, there will be electrodynamical forces arising from the motions of the atoms or molecules.

Each molecule of a solid will, in addition to its internal and translational vibrations, possess a rotational vibration in the field of intermolecular force. As we pass to greater amplitudes of this vibration, we shall come to a point at which a vibration through a finite angle gives place to a complete rotation. The rotation is not of uniform velocity, since irregularities are introduced by the field of force. In a rotating atom or molecule we have the rotation of a system of charges of electricity. The net result is therefore equivalent to a circular current of electricity in the direction of rotation.

Hence, in the case of vibration, the result is the emission of electromagnetic waves; but the force on the atom or molecule varies in direction at each half-phase.

In the case of complete rotation the current and forces are of constant direction : *the atom or molecule may be regarded as a permanent magnet* of moment proportional (except for irregularities) to the angular velocity, and of axis coinciding with axis of rotation.

In general, the axes of these molecular magnets will be distributed at random, so that the solid will exhibit no magnetic properties.

If the solid is placed in a magnetic field, there will be a couple acting on each such magnet, tending to turn its axis of rotation parallel to the lines of magnetic force. Two effects can be detected.

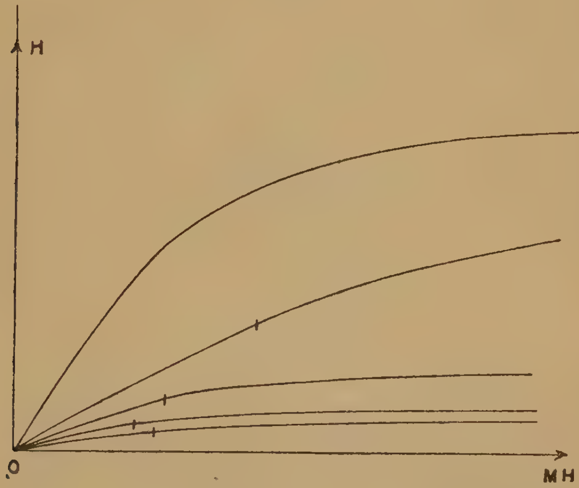
I. The axes of rotation will turn towards the direction of the lines of force. Hence, as in Weber's Theory (Maxwell, § 443), if the axes be a "set," in a particular direction giving the phenomenon of induced magnetism.

Other things being equal, this set will, for sufficiently small values of H, be proportional to H; it will also depend on the rotation of the molecule being proportional to $1/w$.

It follows that the curve of induced magnetization will be given by the superposition of a number of curves such as that given by Weber.

The discontinuities will occur at different points, so that the resultant curve will be continuous.

Fig. 1.



When the magnetic force is removed, the molecules can neither continue to rotate in their present condition, nor can they return immediately to their original state. An intermediate state will ensue, and the time required for the induced magnetism to disappear will depend on the ease with which energy passed between certain degrees of freedom in the solid. The field of intermolecular force may be such that some molecules retain their set for ever. For it may be that some molecules cannot return to their old positions without passing through a position in which their motion is opposed by an intermolecular couple greater than the gyrostatic couple caused by their angular rotation. In the former and more general case, we have residual magnetism; in the latter, permanent magnetism.

II. A further effect of the external field H is seen upon considering that the rotation of the molecules gives rise, virtually, to an electric current. If the current were *real*, the addition of the external magnetic force would give rise to an induced current: in the present case it gives rise to a retardation of the angular velocity about the lines of magnetic force, the velocity being regarded as a vector. It may therefore be regarded as giving rise to a system of magnets of which the direction is opposite to that of the magnetic force.

Hence diamagnetism may be accounted for in the manner of Weber (Maxwell, Treatise, § 838).

§ 39. The great range of values which is known to be possible for K, the coefficient of magnetic induction, can easily be accounted for. Suppose (for the sake of simplicity) that the rotation of a molecule is a "normal" degree of freedom. This will be specified by a subsidiary temperature; and if a be the mean energy, the law of distribution may for illustrative purposes be taken to be

$$\mathrm{E}e^{-\frac{\mathrm{E}}{a}}\,d\sqrt{\mathrm{E}}$$

where E is the energy of the rotation (proportional to w^2).

Let b be the value of E at which the motion changes from oscillatory vibrations to complete revolutions.

In a field of force H a couple acts on this magnet which is proportional (as regards H and w) to Hw. If θ is the angular displacement produced, the couple is also proportional to θw^2. Hence θ is proportional to H/w. This displacement may be regarded as the creation of a new magnet, proportional to $(\mathrm{H}/w)\times w$, and therefore proportional to H, and independent of w. The total *induction* is therefore proportional to

$$\mathrm{H}\int_b^\infty \mathrm{E}e^{-\frac{\mathrm{E}}{a}}\,d\sqrt{\mathrm{E}}\,;$$

and therefore to the area of the curve

$$y=x^2e^{-x^2},$$

which is on the right of the ordinate

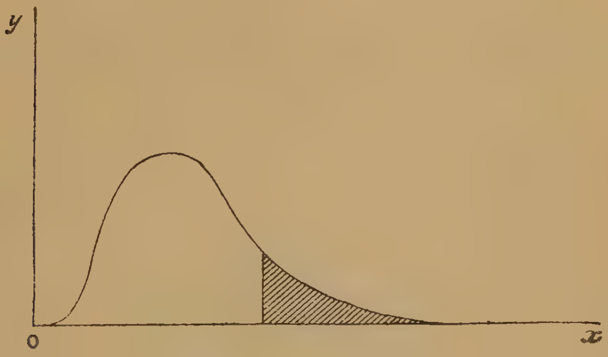
$$x = \sqrt{b/a}.$$

Thus if b is comparable with a, the coefficient k, given by

$$4\pi k = \int_b^\infty \mathrm{E} e^{-\frac{\mathrm{E}}{a}} d\sqrt{\mathrm{E}}$$

will vary rapidly with slow changes in b/a.

Fig. 2.



Since a is the measure of a subsidiary temperature, a may vary enormously from one substance to another.

Calculation of Specific Inductive Capacity.

§ 40. Under a steady field of electric force C every ion at the surface of any atom is in equilibrium under the force, the displacement-potential of the atom to which it belongs, and the potential arising from other atoms. Neglecting the latter, the displacement-potential at every point of the surface of any atom must be Ex ; or if R is the radius of the atom,

$$\mathrm{E}_1 \mathrm{R} \cos\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

At all points outside the atom this displacement-potential satisfies Laplace's equation, and it is continuous with (34) at $r = \mathrm{R}_1$. The general solution is therefore

$$\mathrm{E} \cos\theta \mathrm{R}_1{}^3/r^2.$$

If there are Ndv such atoms in a small element of volume dv, the total displacement-potential at an external point will be

$$\mathrm{NE} \cos\theta \mathrm{R}_1{}^3 dv/r^2 \quad \text{or} \quad \mathrm{ENR}_1{}^3 x/r^3.$$

The specific inductive capacity of a medium composed of such atoms will therefore be given by

$$\frac{k-1}{k+2}=\mathrm{NR}_1^3.$$

For a gas this gives

$$k=1+9\theta/4\pi,$$

where θ is the fraction of the total volume which is occupied by atoms.

It is clear that this is of the right order of magnitude. For oxygen, hydrogen, nitrogen at the density of the air the refractive index is roughly 1·00025 *, giving

$$k=1{\cdot}0005.$$

Substituting this value in the formula just found for k (and neglecting the difference between atoms and molecules, since this will not affect the order of magnitude of the quantities concerned), we get

$$\theta=\cdot0007.$$

Now the density of liquid oxygen, nitrogen, &c., is roughly 1000 times that of air, so that the value of θ just found will be at any rate comparable with the true value.

Dielectrics, Conductors, and Electrolytes.

§ 41. It will be seen that the foregoing theory of the specific inductive capacity of a dielectric is virtually that of Mossotti †. The atoms or molecules must not be regarded as perfect conductors, but they arrange themselves so that their external surfaces are equipotentials, and therefore behave like conductors to all external points.

In a solid body each ion will be in equilibrium under the forces arising from all the ions in the solid. In the case of some substances, the solid may be regarded as a collection of atoms, or molecules, each individual atom retaining its identity; whereas for other substances the body must simply be regarded as a confused mixture of ions which have placed themselves in equilibrium.

The difference is that between a dielectric and a conductor. If the former body is placed in an electric field, the molecules will arrange themselves so that their surfaces are equipotentials, and we have a dielectric of which the theory of Mossotti gives a good account.

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* Preston, 'Theory of Light,' p. 137.

† Maxwell, Elect. and Mag. § 62.

When a body of the second sort is placed in an electric field, the ions (possibly all ions, or possibly only the ions of the outermost layer) will be free to move from one molecule to another, and will therefore arrange themselves so that the whole surface of the body is an equipotential. In one half of the body there would be an excess of negative ions, in the other half an excess of positive ions: the former is the so-called "induced charge" of negative electricity, the latter of positive. Before the ions have taken up their equilibrium positions there will be a flow of ions through the body, and this is a "current of electricity."

A third class of body can be imagined in which the ions are closely bound into atoms, but the bond between the various atoms of a molecule is very slight: this is the class of electrolytes. A current in this case involves an actual transfer of atoms through the electrolyte.

Consider, for instance, the electrolysis of hydrochloric acid. The hydrogen atom has a convergence of force equal and opposite to that of a negative ion. Every pair of hydrogen atoms as they arrive at the cathode will combine with two of the negative ions which have been conveying the current through the metal cathode, and will together form a neutral hydrogen molecule. So also at the anode, the pairs of chlorine atoms combine into molecules, and in doing so liberate the ions which are to carry the current away from the anode. Faraday's Laws of electrolysis follow at once.

Conclusion.

§ 42. This concludes the comparison between the phenomena which are to be expected from our hypothetical matter and those which are observed to occur in nature. It must be left for individual judgments to decide whether the test afforded in this way is sufficiently strict to be worth anything; and if so, to decide what is the measure of probability that our hypothetical matter gives a clue to the structure of actual matter.

§ 43. In conclusion, reference may be made to a question which demands an answer in the case of this, as in the case of every other hypothesis which attempts to place the structure of matter on a purely electrical or æthereal basis. The only difference which the æther-equations of electricity can recognize between a negative and a positive charge of electricity is a mere difference of sign; so that if we regard a negative ion as an æther-structure, we are inevitably led to regard the possibility of positive ions differing from negative ions only by a difference of sign. On the other hand, the predominance of the negative ion in most material phenomena, and in the emission of light (as evidenced by the Zeeman Effect) seems to suggest the view that positive and negative ions differ in something more than mere sign. Any attempt to explain matter in terms of æther must therefore face the problem of reducing what appears to be a difference in quality to a difference in sign only.

We can explain these facts, in terms of our present theory, by supposing (§ 26) that the outermost shell of ions in any atom consists exclusively of negative ions, but there still remains the question as to why it is that the positive ions rather than the negative are excluded from the outermost shells of the atom; we have not yet removed the essential difference in quality between positive and negative ions.

We cannot suppose that all atoms with positive ions at the surface are unstable; for corresponding to any stable arrangement with negative ions at the surface, there must be a stable arrangement which is exactly the same except that the sign of every ion is changed. If an ordinary atom is referred to as a positive atom, this other kind of atom may be referred to as a negative atom.

Let us refer to the atoms of the various chemical elements as A, B, C, ..., and let the imaginary corresponding negative atoms be referred to as A′, B′, C′, ... In order that a system of chemical elements A, B, C, ... may have a permanent existence it is not only necessary that the individual atoms A, B, C, ... shall each be statically stable, but also that when any atom A meets another atom B, the atoms A and B shall not lose their identity. Now the forces exerted between A and B when in proximity will arise mainly from that part of the potential-function which represents the divergence of the forces exerted by the ions near the point of closest approach from those calculated on the ordinary electrostatic law, and will possibly depend largely upon the signs of the ions in these outermost shells. Thus if A and B do *not* unite so closely as to lose their separate identity, it is not difficult to imagine that A′ and B would be drawn together until a complete rearrangement of ions had been effected and a new atom or atoms formed. If this supposition be accepted it will be clear that a condition that a system of elements should have a permanent existence is that the outermost layers of all the atoms shall be of the same sign. We can imagine a number of positive and negative ions initially scattered at random in space to condense into matter of both kinds, but whenever a collision takes place between two atoms of different kinds, the result is a rearrangement of parts, until finally only one class of matter is left in the field.

This last suggestion is of a very speculative kind; but it may be noticed that if matter is an æther-structure, and if the difference between positive and negative electricity only enters in the æther-equations through a mere difference of sign, then the observed difference between the relations of the two kinds of electricity to material phenomena can only arise from a difference in the initial conditions, such as that just described.

12

LIX. *The Spectrum of Cyanogen.* *By* E. C. C. Baly, *F.I.C., and* H. W. Syers, *M.A., M.D.*[*] (Communicated by Prof. W. Ramsay, F.R.S.)

In a recent paper in the Philosophical Magazine on the Spectra of Carbon[†], Professor Smithells pointed out the desirability of observing the vacuum-tube spectrum of cyanogen, with particular reference to the presence or absence of the spectra of carbon, inasmuch as their absence would materially support the explanation he puts forward as to their origin, namely, that the carbon-oxide spectrum is due to carbon dioxide, and the Swan spectrum to carbon monoxide, while the line spectrum is due to the element carbon.

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[*] Read June 28, 1901.

[†] Phil. Mag. April 1901.

One of us in a previous paper[*], some years back, in dealing with the stratification of the electric discharge, described experiments which had been made on mixtures of hydrogen and carbon dioxide and referred to the spectra seen as those of hydrogen and carbon dioxide. This has since been criticised severely[†], because in the general opinion of spectroscopists carbon dioxide has no spectrum at all.

A great number of experiments, however, had been previously carried out with a view of obtaining a mixture of hydrogen and carbon monoxide, or rather a mixture which showed only the Swan spectrum together with that of hydrogen. This was found at the time to be impossible, as the Swan spectrum was at once changed into the carbon-oxide spectrum.

In order to obtain the Swan spectrum in a pure state, it was found necessary to fill a vacuum-tube with pure carbon monoxide, using the greatest precautions to eliminate all impurities, as the smallest trace of oxygen at once changed the spectrum to the carbon-oxide spectrum, which itself was always obtained when carbon dioxide was used.

These results were not published at the time as they did not actually bear on the work in hand; but in view of Professor Smithells's recent paper, it seems worth while to describe them and others more recently carried out, since they support very strongly the view he puts forward. There seems, indeed, no room for doubt that the true explanation of these spectra is that they are due to carbon monoxide and dioxide respectively, but at the same time it is easy to see how confusion could arise. In the first place, there is the extreme difficulty of obtaining a vacuum-tube containing pure carbon monoxide; and in the second place, a very small quantity of carbon dioxide in a mixture gives a very decided spectrum, and can easily mask that of carbon monoxide. These two facts can account for all the difficulty connected with the vacuum-tube spectra of the gases, because under ordinary circumstances carbon monoxide is changed so far into carbon dioxide that it shows none, or only very little, of the Swan spectrum, but practically entirely the carbon-oxide spectrum. Naturally, therefore, the carbon-oxide spectrum was attributed to carbon monoxide.

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[*] Baly, Phil. Mag. xxxv. p. 200 (1893).

[†] Kayser, *Handbuch der Spectroscopie*, p. 198.

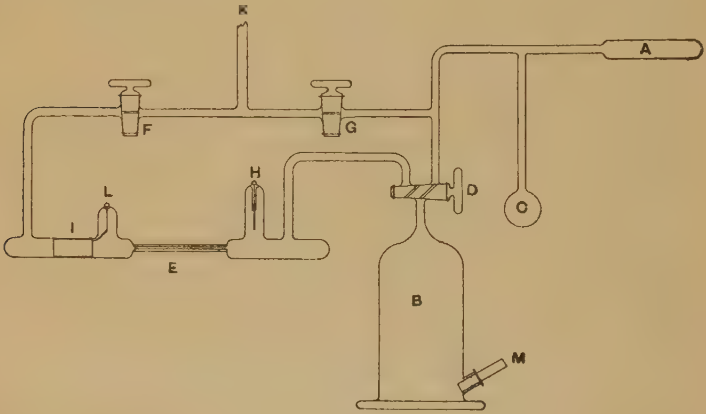
As Professor Smithells has shown, if proper precautions are taken, then carbon monoxide gives the Swan spectrum, and when pure only the Swan spectrum. The chief difficulty lies in removing all the condensed air from the walls of the vacuum-tube, and all the occluded gases from the electrodes. This can be done quite easily by exhausting as far as possible, keeping the discharge passing and heating the vacuum-tube with a Bunsen-burner. The carbon monoxide must be made from formic acid and sulphuric acid, and should preferably be let into the vacuum-tube directly from the generating apparatus.

Even with the above precautions, the first admission of the gas often gives no Swan spectrum; but after re-exhaustion and re-admission once or twice more, the Swan spectrum is seen unmixed with the carbon-oxide spectrum. This experiment has been repeated very many times in various ways, and with always identically the same result.

It is interesting also to note that, under certain conditions, the carbon monoxide deposits carbon under the influence of the discharge; this is always at once accompanied by a change in the spectrum to the carbon-oxide spectrum. Again, the admission of a small trace of oxygen into a vacuum-tube showing the Swan spectrum, instantaneously changes it to the carbon-oxide spectrum. These facts are strongly confirmatory of the theory.

As regards the carbon-oxide spectrum, this is invariably obtained when the electric discharge is passed through either carbon dioxide itself, or a mixture of carbonic oxide and oxygen.

As Professor Smithells has pointed out, considerable support would be gained to the above view of the carbon spectra, if it could be shown that a carbon compound such as cyanogen gives no Swan spectrum when under the influence of the electric discharge. Smithells was unable to satisfy himself as regards this, owing to the inherent difficulties in working with cyanogen; but, by taking similar precautions as were described above, we have succeeded in filling vacuum-tubes with cyanogen which showed no trace of either of the carbon spectra, but only a very beautiful and characteristic cyanogen spectrum. In these experiments, the first difficulty to be overcome was in connexion with the purity of the cyanogen itself. This was overcome as follows:—About half a litre of the gas was prepared as pure as possible by heating mercuric cyanide, and this was then frozen in a small bulb immersed in liquid air. The bulb containing the cyanogen was then exhausted as far as possible with a mercury-pump, and the liquid air being then removed, the cyanogen was allowed to boil off into a gas-holder. A second difficulty was the very rapid polymerization to paracyanogen, which takes place when the discharge is passed through the gas; this was, however, surmounted by allowing a slow stream of cyanogen to flow into the vacuum-tube.



The apparatus used is shown in the figure, where A is the tube containing the mercuric cyanide, and B a mercury gas-holder to which was fitted a reservoir and indiarubber tubing on the tube M, while C is the bulb in which the gas was frozen. The gasholder B was provided with a three-way stopcock D, one arm of which was connected to the cyanogen-supply apparatus, and the other to one end of the vacuum-tube E. The other end of the vacuum-tube was connected to the pump through the tap F, and the cyanogen supply apparatus was also connected to the pump through the tap G. On account of the very rapid deposition of paracyanogen on the walls of the vacuum-tube when the discharge is passed through cyanogen, it was found impossible to examine the spectrum of the discharge in the usual way, as the brown deposit became rapidly quite opaque. It was necessary therefore to observe the discharge "end on," and the tube was arranged as shown in the diagram. The electrode I was made in the shape of a hollow cylinder of sheet-aluminium, which fitted tightly into the tube and enabled the spectrum of the negative glow to be examined if desired. Connexion was made with I by a platinum wire sealed in at L. The other electrode was of aluminium wire of the usual design, and was sealed in at H. Connexion was made with a mercury-pump through the tube K, and in this way both parts of the apparatus could be separately exhausted.

The first stage of course was to prepare the pure cyanogen, which was carried out as follows:—The gasholder B was nearly emptied of mercury, which was run into the reservoir and the indiarubber tube tightly clipped. The three-way tap D was turned so as to connect the gasholder with the cyanogen apparatus, and the whole was exhausted as far as possible through the tap G. In this way all the condensed gases were removed from the cyanide of mercury and the walls of the gasholder. The tap G was then closed, and the cyanide in A strongly heated until sufficient cyanogen had collected to fill the gasholder. The bulb C was then immersed in liquid air, and all the cyanogen frozen therein; the tap G being then again opened, any gas left unliquefied was pumped away, it being found that the exhaustion could be carried very high, as the solid cyanogen has such an extremely low vapour-pressure at the temperature of boiling air. The tap G was then again closed, and the cyanogen allowed to boil back into the gasholder.

The second stage was to exhaust the vacuum-tube as far as possible, with the discharge passing during the whole time, in order to remove every trace of gas from all parts of the tube.

When this process had been effectively carried out, small quantities of cyanogen were admitted and pumped out again, the spectrum being examined after each admission. At first the carbon spectra were seen together with the nitrogen spectra, showing undoubtedly that oxidation of the cyanogen was taking place. This, however, became less and less evident, and finally we were able to obtain a spectrum absolutely free from the carbon and nitrogen spectra. The spectrum obtained was extremely beautiful, and differs from the flame-spectrum of cyanogen. It presents a series of equidistant flutings through the whole of the red and yellow, somewhat recalling those of the positive band-spectrum of nitrogen. The cyanogen bands are, however, much wider than the nitrogen bands, and do not show the characteristic break in the orange seen in the nitrogen spectrum. The flutings under higher dispersion are of course split into series of very fine lines.

The polymerization of the cyanogen was so rapid as only to allow the observations to last a few seconds after the admission of the gas. We succeeded, however, in overcoming this difficulty by allowing a constant slow stream of cyanogen to pass into the tube, and in this way were able to take careful observations. That the brown deposit on the vacuum-tube is paracyanogen, can easily be proved by its volatility at a high temperature.

It is worth while also to point out, that the admission of oxygen or air into the vacuum-tube during the experiments was at once attended by the appearance of the carbon spectra.

In conclusion, these experiments tend to prove that

(1st) The Swan spectrum is not produced by a carbon compound which does not contain oxygen; whence it follows that

(2nd) The Swan spectrum is that of an oxide of carbon as it is only produced by carbon monoxide; and as this spectrum is changed at once into the carbon-oxide spectrum by admission of oxygen or by intense electric discharge, and, further, as the carbon-oxide spectrum is invariably given by carbon dioxide, there can be no doubt that

(3rd) The Swan spectrum is that of carbon monoxide, and the carbon oxide spectrum that of carbon dioxide.

We wish to express our indebtedness to Professor Ramsay for the great interest he has taken in the experiments.

Spectroscopic Laboratory,
University College, London, June 1901.

DISCUSSION.

Mr. GASTER said that this paper might throw more light on the question of the arc, where cyanogen is present from the cyanic acid formed together with the other products of combustion such as carbon monoxide and dioxide. The opinion as to what the spectrum of the arc really represented was, so far as he knew, not definitely settled yet, but the spectrum of cyanogen, which differs from that of any hydrocarbon or carbon monoxide or carbon dioxide, is also present in the arc, together with the other ones. We ought to be able, with the aid of the spectroscope, to study the arc phenomena, and define, at least in general outlines, the different chemical changes which accompany those phenomena, as, for instance, the "hissing" of the arc. Those who wish to improve the efficiency of the arc, for which in his opinion there is plenty of scope, should make use of the spectroscope, which they will probably find to be of considerable advantage.

LX. *On the Effect of a High Frequency Oscillating Field upon the Electrical Resistance of Selenium and Tellurium.* *By* S. A. F. White, *M.A.*

[Abstract.]

A piece of selenium, exposed to the action of the field produced between two insulated metal plates attached to the secondary terminals of a Tesla coil, has its electrical resistance increased. A specimen whose original resistance is low (of the order 100 to 1000 ohms), on exposure to a strong field or to the actual passing of a spark from one of the plates, is immediately and permanently converted into one of high resistance (of the order megohms).

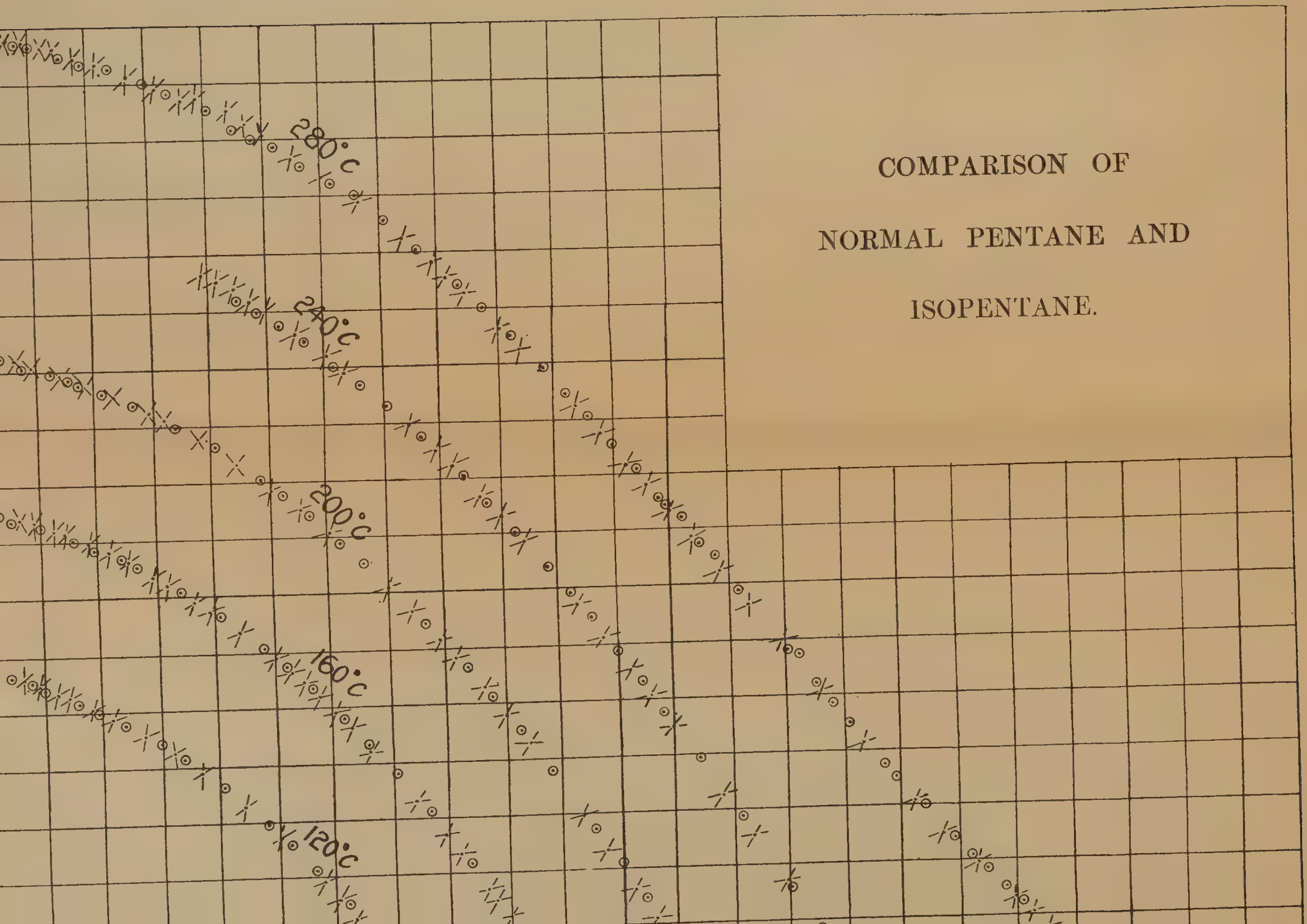
When in this condition or if the original resistance of the specimen is high, the effect of the field is to notably increase the resistance, but it may again be lowered by exposure to light or by alternate heating and cooling.

The effect of a rise of temperature appears to be two-fold: the conductivity of a piece of low resistance is decreased while that of a piece of high resistance is increased.

The effect of the oscillating spark upon a piece of tellurium is to temporarily decrease its electrical resistance.

A rise of temperature produces a large decrease of electrical resistance, but repeated heated and cooling permanently increases the resistance of the specimen. This latter effect depends upon the material employed for the electrodes. It is much greater with copper than with platinum electrodes. In the condition of increased resistance, the effect of the spark in producing a temporary fall of resistance is much more marked.

COMPARISON OF NORMAL PENTANE AND ISOPENTANE.



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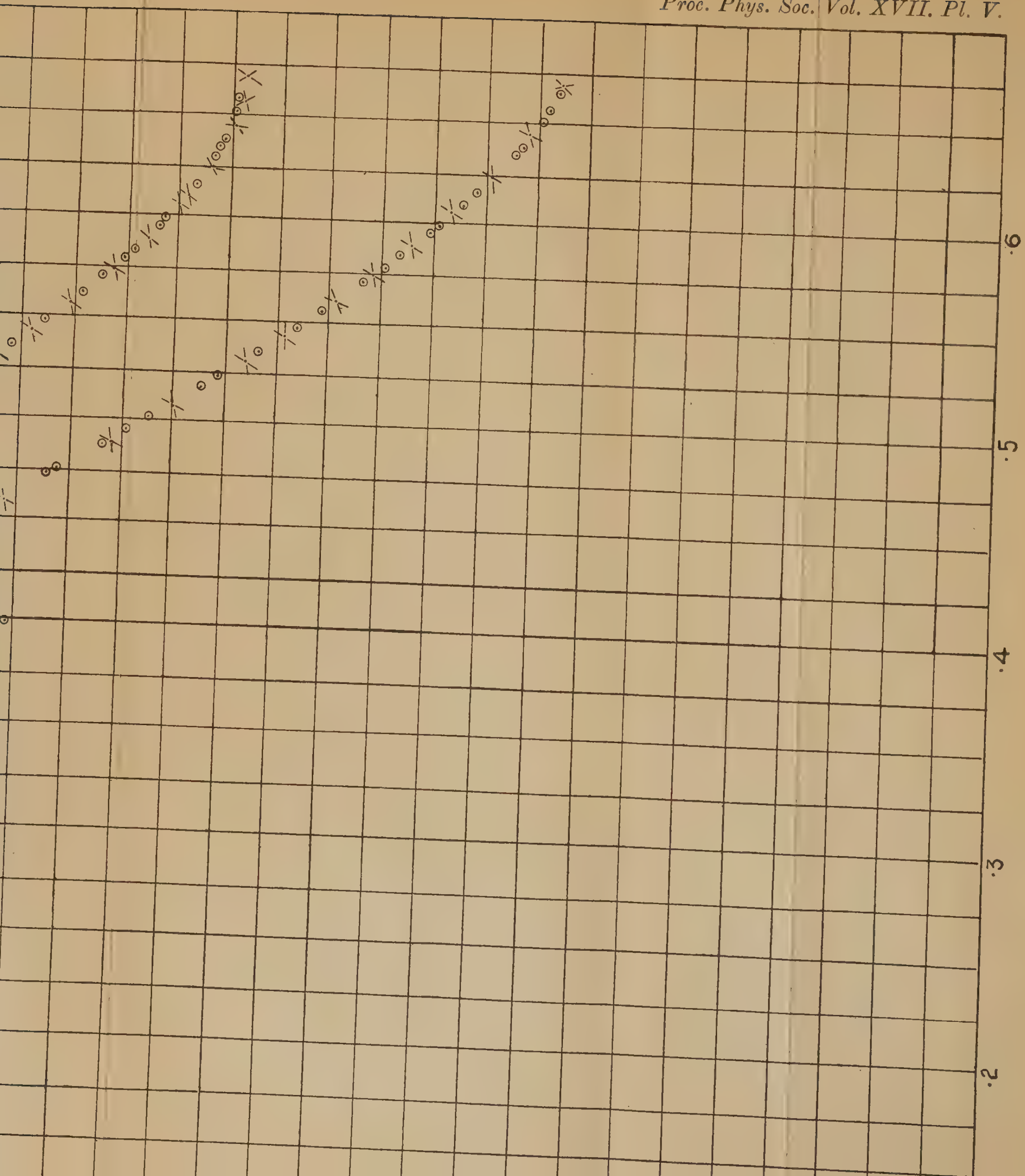
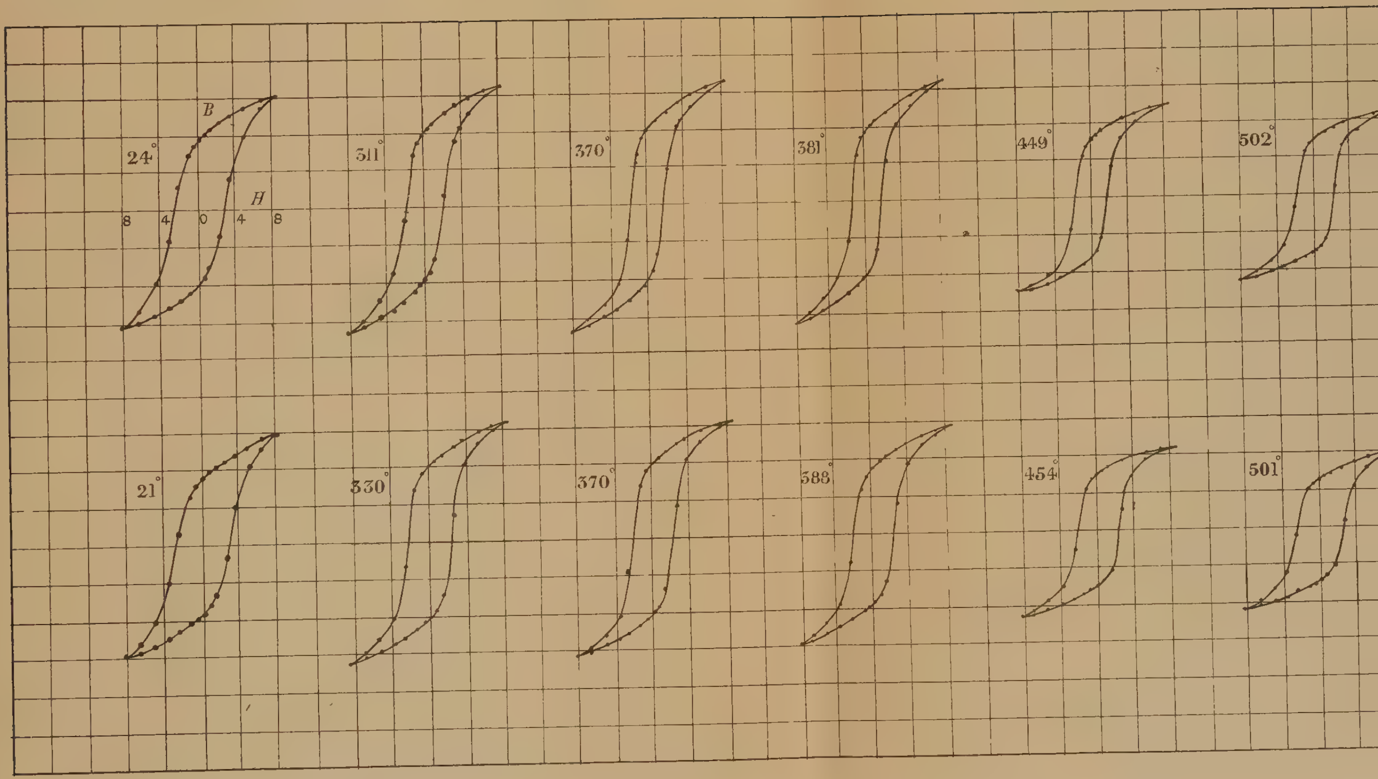
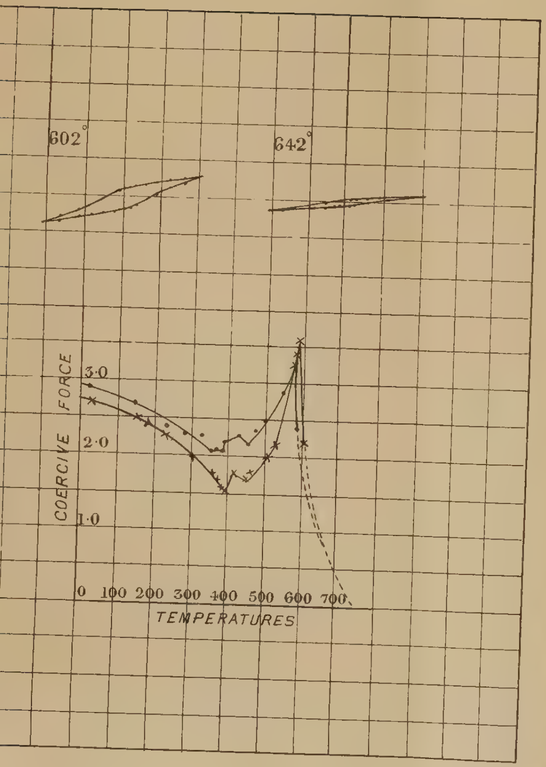


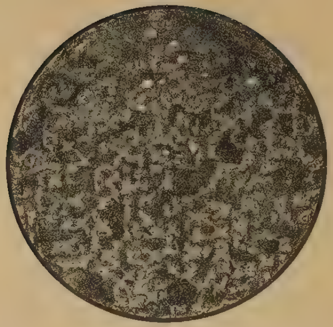
TEMPERATURE RISING →



TEMPERATURE FALLING ←

Proc. Phys. Soc. Vol. XVII. Pl. VI.





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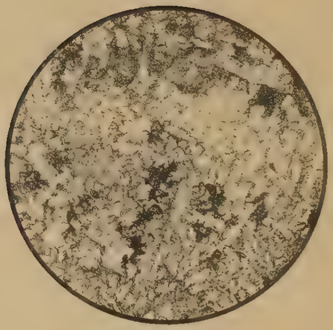

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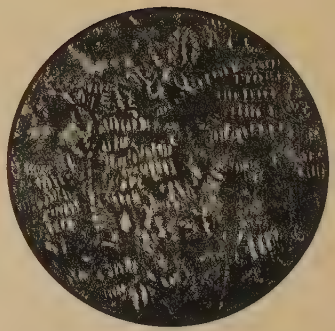


C

Mintern Bros. lith.

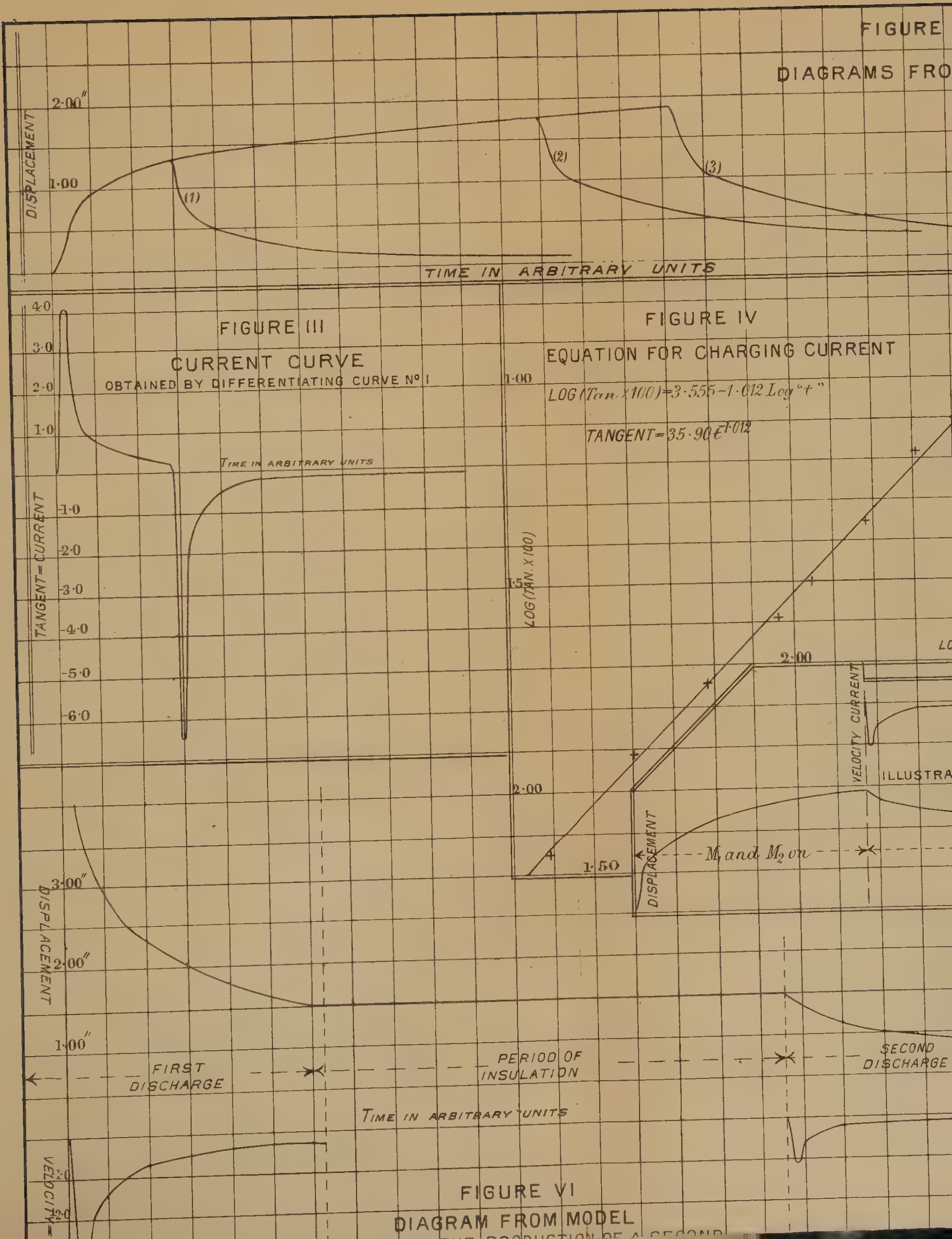


FIGURE III

CURRENT CURVE

OBTAINED BY DIFFERENTIATING CURVE No I

FIGURE IV

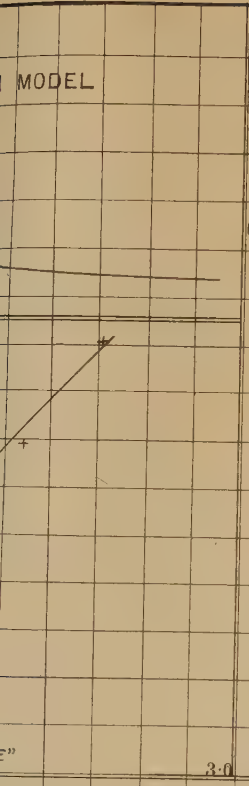
EQUATION FOR CHARGING CURRENT

$LOG\,(Tan \times 100) = 3\cdot555 - 1\cdot012\,Log\,“t”$

$TANGENT = 35\cdot90\,\epsilon^{1\cdot012}$

FIGURE VI

DIAGRAM FROM MODEL



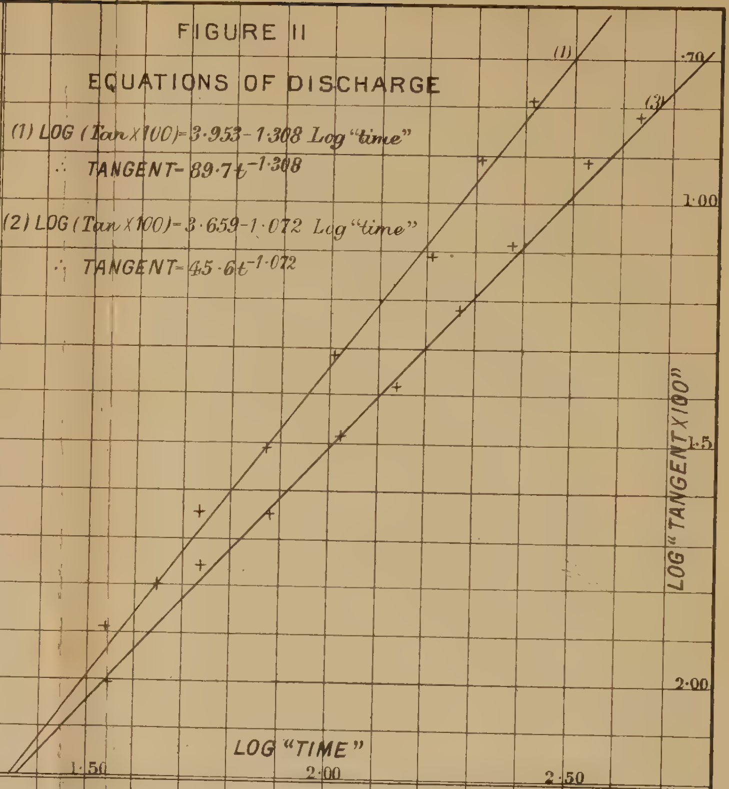


FIGURE II

EQUATIONS OF DISCHARGE

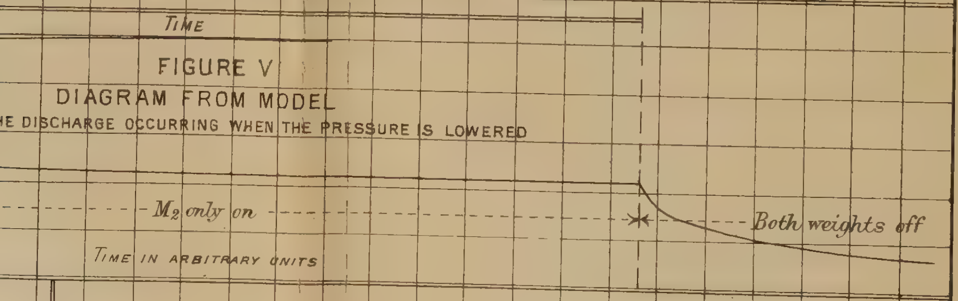
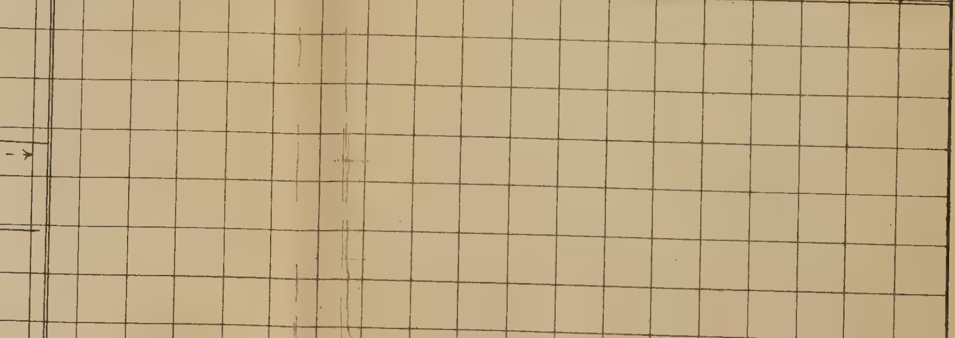


FIGURE V

DIAGRAM FROM MODEL

HE DISCHARGE OCCURRING WHEN THE PRESSURE IS LOWERED



December 8th, 1899.

Meeting held at the City and Guilds' Technical College, Finsbury, on the invitation of Prof. S. P. Thompson.

Professor G. Carey Foster, Vice-President, in the Chair.

Papers:

- On Cylindrical Lenses, by Prof. S. P. Thompson, D.Sc., F.R.S.
- On Exact Formulæ for Lenses, by Mr. T. H. Blakesley, M.A.
- On an Organic Compound of great Double-Refraction, by Prof. Thompson.
- Exhibition of a Transmission Dynamometer by Prof. Dalby.

January 26th, 1900.

Meeting held at Burlington House.

Professor Oliver Lodge, President, in the Chair.

Messrs. S. W. Richardson and J. A. Tomkin were elected Fellows.

Papers:

- On some Developments in the use of Price's Guard-Wire in Insulation Tests, by Prof. W. E. Ayrton, F.R.S., and Mr. Mather.
- On the Reflexion and Transmission by Condensers of Electric Waves along Wires, by Mr. E. H. Barton, D.Sc., and Mr. Lownds.
- Exhibition of some Glow Lamps made into Mirrors by the application of too much Voltage, by Mr. R. Appleyard.

Annual General Meeting.

February 9th, 1900.

Professor OLIVER LODGE, President, in the Chair.

The following Report of the Council was read by the Secretary:—

Since the last Annual General Meeting of the Society thirteen meetings have been held. One of these, that of November 10th, was held at the Central Technical College, Exhibition Road, on the invitation of Prof. Ayrton, and one, on December 8th, at the City and Guilds' Technical College, Finsbury, on the invitation of Prof. S. P. Thompson. All the other meetings were held in the rooms of the Chemical Society at Burlington House.

Thirteen new Fellows have been elected into the Society; and the following names have been removed from the list by death:— John Donaldson, Sir E. Frankland, Dr. J. L. Howard, Prof. D. E. Hughes, and S. O. Roberts. There have also been three resignations. Short memoirs of some of the above will be published in the Society's 'Proceedings.'

Two Hon. Fellows, Profs. Wiedemann and Bunsen, have also died during the year.

A special sub-Committee of the Council was appointed early in the year to consider the conduct of the Society's meetings, and to endeavour to find means to make them more attractive to the Fellows. This committee made a number of recommendations to the Council, some of which were adopted. These were embodied in a circular which was sent out to all Fellows of the Society at the commencement of the present Session.

One of the most important of these recommendations was that meetings should frequently be held at other places than Burlington House, so that experiments might be more easily shown and larger apparatus inspected.

Two such meetings have since been held, and invitations have been received for several more.

In the Annual Report last year the following sentence occurred: "It is confidently hoped that it will be possible to arrange for the permanent production of 'Science Abstracts' on a scale at least as extensive as the present."

Your Council is happy to report that this hope has been fulfilled. An agreement for three years has been come to with the Institution of Electrical Engineers, and will shortly be signed, under which 'Science Abstracts' will continue to be published by a Committee of the two Societies; and it has already been found possible to increase the scope of the publication, as will be seen on inspection of the January number which has been for some days in the hands of Fellows.

The Report of the Council was adopted.

The Report of the Treasurer was read and adopted.

The election of Officers and other Members of Council then took place, the new Council being constituted as follows:—

President.—Prof. OLIVER J. LODGE, D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President.—Dr. J. H. GLADSTONE, F.R.S.; Prof. G. C. FOSTER, F.R.S.; Prof. W. G. ADAMS, M.A., F.R.S.; Lord KELVIN, D.C.L., LL.D., F.R.S.; Prof. R. B. CLIFTON, M.A., F.R.S.; Prof. A. W. REINOLD, M.A., F.R.S.; Prof. W. E. AYRTON, F.R.S.; Prof. G. F. FITZGERALD, M.A., F.R.S.; Prof. A. W. RÜCKER, M.A., F.R.S.; Sir W. DE W. ABNEY, K.C.B., D.C.L., F.R.S.; SHELFORD BIDWELL, M.A., LL.B., F.R.S.

Vice-Presidents.—T. H. BLAKESLEY, M.A.; C. VERNON BOYS, F.R.S.; Prof. J. D. EVERETT, D.C.L., F.R.S.; G. GRIFFITH, M.A.

Secretaries.—H. M. ELDER, M.A.; W. WATSON, B.Sc.

Foreign Secretary.—Prof. S. P. THOMPSON, D.Sc., F.R.S.

Treasurer.—Prof. H. L. CALLENDAR, M.A., F.R.S.

Librarian.—W. WATSON, B.Sc.

Other Members of Council.—Prof. H. E. ARMSTRONG, Ph.D., LL.D., F.R.S.; Dr. E. ATKINSON; WALTER BAILY, M.A.; Prof. R. T. GLAZEBROOK, M.A., F.R.S.; E. H. GRIFFITHS, M.A., F.R.S.; S. LUPTON, M.A.; Prof. J. PERRY, D.Sc., F.R.S.; J. SWINBURNE; R. THRELFALL, M.A., F.R.S.; J. WALKER, M.A.

Votes of thanks were passed to the Auditors, the Officers and Council, and to the Chemical Society.

The President then delivered an Address, which will appear in the 'Proceedings.'

THE TREASURER IN ACCOUNT WITH THE PHYSICAL SOCIETY, FROM JANUARY 1ST, 1899, TO DECEMBER 31ST, 1899.

Dr.	£	s.	d.	£	s.	d.
Jan. 1, 1899. Balance in the Bank				384	14	6
Entrance-Fees	13	0	0			
Subscriptions for 1898 & previous	32	10	0			
" 1899	337	18	4			
Extra Subscriptions for 1899	28	7	0			
Subscription for 1900	2	2	0			
				413	17	4
Life Composition				31	10	0
Dividends:—						
Furness Debenture Stock	15	9	4			
Metropolitan Board of Works	6	15	4			
Lancaster Corporation Stock	9	14	4			
South Australian 3½ per cent.	8	12	0			
Midland Railway	38	13	4			
				79	4	4
Sales of publications	36	19	5			
Balance from Dinner	4	12	0			
				41	11	5
Cheque not yet presented				2	14	11
Balance due to the Treasurer				4	5	7
				£957	18	1

Cr.	£	s.	d.	£	s.	d.
Balance paid to the Treasurer, Jan. 1, 1899				13	14	5
Abstracts: balance for 1898	70	0	0			
" 1899	310	0	0			
				380	0	0
Taylor and Francis, for printing:—						
Proceedings	90	16	9			
Distribution	14	14	6			
Separate Copies	14	3	6			
Miscellaneous Printing	40	11	2			
				160	5	11
Asiatic Society, annual rent of name-plate				2	2	0
Chemical Society (2 years)				40	8	6
Attendance				2	3	0
Purchase of £130 Lanc. Corp. Stock				133	9	0
Waterlow: engrossing address				3	3	0
Reporting				23	13	11
Binding				12	1	10
Commission on Cheques					2	9
Petty Cash:—						
Mr. Elder	2	14	11			
Mr. Watson	2	1	10			
Dr. Atkinson	2	3	9			
				7	0	6
Balance in the Bank				179	13	3
				£957	18	1

EDMUND ATKINSON, *Treasurer.*

Audited and found correct.

WILLIAM BARLOW, } *Auditors.*
EDWARD F. HERROUN, }

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, December 31, 1899.

Assets.	£	s.	d.	£	s.	d.
Subscriptions due, estimated				30	0	0
£400 Furness 4 per cent. Debenture Stock	456	0	0			
£1000 Midland 4 per cent. Preference Stock	1194	0	0			
£200 Metropolitan Board of Works 3½ per cent. Stock	217	0	0			
£400 Lancaster Corporation 3 per cent. Stock	360	15	8			
£254 2*s.* 9*d.* New South Wales 3½ per cent. Inscribed Stock	249	7	5			
				2477	3	1
Balance in the Bank				179	13	3
Guarantee Fund, on Deposit				434	0	7
				£3120	16	11

Liabilities.	£	s.	d.
Balance due to the Treasurer	4	5	7
Cheque not presented	2	14	11
Abstracts: due to the Joint Committee	40	0	0
Printers	84	15	6
Balance	2989	0	11
	£3120	16	11

EDMUND ATKINSON, *Treasurer.*

Securities examined and found correct.

WILLIAM BARLOW, } *Auditors.*
EDWARD F. HERROUN }

Gustav Heinrich Wiedemann was born in Berlin in 1826. At the age of 18 he entered the University of his native city, having already resolved to devote his life to the pursuit of physics. With this object in view, he gave his first years at the University to the study of mathematics and chemistry before concentrating his attention on what was to be his permanent occupation. Among his teachers at Berlin were Dirichlet, Joachimsthal, Heinrich Rose, Sonnenschein, Mitscherlich, Dove, and Magnus. Among his contemporaries at the University was Helmholtz, and a cordial friendship began between the two young physicists which was interrupted only by death. There was in these days no chair of mathematical physics in Berlin, but the two friends studied the subject on their own account and read together, among other works, Poisson's writings on elasticity.

In 1850 Wiedemann was admitted a *Privatdocent* of his University, and began to lecture on special branches of physics. Beetz and Clausius were *Privatdocents* of physics at Berlin at the same time. Wiedemann's first Professorship was at Basel, where he held the Chair of Physics from 1854 till 1863. In the latter year he was appointed Professor of Physics in the High Technical School at Brunswick; and in 1866 he accepted a similar appointment at Carlsruhe in succession to the elder Eisenlohr. In 1871 he was called to the University of Leipzig as Professor of Physical Chemistry; afterwards, on Hankel's resignation of his Chair in 1887, he became Professor of Physics in the same University. He retained this post practically to the end of his life: he obtained a dispensation from lecturing for the winter session 1898–9, and resigned his Professorship in the spring of 1899. He did not, however, live to enjoy the rest he had so well earned, for he died on the 24th March, 1899.

Among the subjects dealt with in Wiedemann's numerous experimental investigations were electric endosmose, the comparative thermal conductivity of metals, the magnetic rotation of the plane of polarization of light, the dissociation-pressure of hydrated crystals, the magnetic properties of salts both crystallized and in solution, especially salts of the magnetic metals, the electric discharge through rarefied gases, the magnetization of steel, specially the relation between permanent and temporary magnetization, the influence of temperature, and the effects of reversal of magnetization. In connexion with these last investigations he experimented on the torsion of wires, and demonstrated a very remarkable parallelism between the laws of magnetization and those of torsion. Another important piece of work which occupied much time was the determination of the relation between the ohm and the mercury unit of resistance. This was carried out with the help of a large coil that had been prepared for the purpose by Wilhelm Weber and Zöllner. The result arrived at was 106·265 cm. as compared with 106·3 cm., the value officially adopted by the Board of Trade, the German Government, and by the International Electric Congress at Chicago.

Wiedemann's name is, however, probably even better known in connexion with his literary labours than for his experimental work. In 1861 he brought out the first edition of his '*Lehre vom Galvanismus und Elektromagnetismus.*' This was intended to be, for current-electricity, a counterpart of the celebrated work of P. T. Riess, '*Die Lehre von der Reibungselektricität,*' published in 1853. The completeness and accuracy of this work are too well known to all physicists for it to be needful to dwell upon them. A second edition under the same title appeared between 1872 and 1874, but the progress of discovery made the separate treatment of current-electricity apart from electrostatics every year more and more unsatisfactory; and Wiedemann's third edition appeared in 1884 as '*Die Lehre von der Elektricität.*' The fourth and last edition was completed only a few months before the author's death. The production and revision of this work, derived almost entirely from direct consultation of original memoirs, must have involved enormous labour continued for about 40 years, for each edition gives a practically exhaustive representation of the science up to the date of its completion: of each it may be said, that whatever was not included in it was not as yet a part of the science. In 1877 Wiedemann undertook another arduous task involving not only much labour but calling for the constant exercise of judgment, tact, and impartiality. This was the editing of the '*Annalen der Physik und Chemie,*' which had been conducted for fifty years by Poggendorff.

Wiedemann combined with his immense knowledge of physics great learning in many other directions. Personally, his unassuming geniality and kindliness of disposition endeared him to his friends. He was a striking instance of the steadfastness and single-hearted devotion which have made German science and learning what they are. He was elected an Honorary Member of this Society in February 1888, and a Foreign Member of the Royal Society in 1884.

Professor David Edward Hughes, F.R.S., was born in London in 1831; his parents emigrated to the United States in 1838. He became Professor of Music in 1850, and afterwards Professor of Natural Philosophy, in the Bardstown College, Kentucky. For his very famous and much used printing telegraph, invented in 1854, he received decorations from almost every European government. He invented the microphone and the induction-balance, and made many important experimental investigations in magnetism. He was awarded the Royal Medal of the Royal Society in 1885. He was a President of the Institution of Electrical Engineers in 1886.

Robert Wilhelm Bunsen, born on March 31st, 1811, at Göttingen, died at his residence in Heidelberg on August 16th, 1899. From the year 1833, when he became *Privatdocent* in the University of his birth-place, until the year 1889, when he retired from the Professorship of Chemistry at Heidelberg, Bunsen's whole life was devoted to the service of science. Not only as an investigator and as an experimentalist of the first order, but perhaps even more as a great teacher, he has conferred upon science benefits which it is difficult to overestimate. His experimental power was strikingly shown in the construction of new apparatus, always admirably adapted to the uses for which it was designed. His methods were universally characterized by exactitude, and by a careful determination of the experimental error attaching to each. This is especially shown in his work on gasometry, which contains a description of the methods of measuring gaseous volumes and of estimating the constituents of gaseous mixtures with a degree of accuracy formerly undreamt of, and since never excelled. His investigations on the limits of the laws of the absorption of gases by liquids, originally enunciated by Dalton and Henry, may be cited as another example of Bunsen's characteristic work. Although including research in almost every branch of chemical science, Bunsen's chief interests undoubtedly lay in the physico-chemical direction; and so strong was his belief respecting the close connexion between chemistry and physics, that he was in the habit of saying that a chemist who was not a physicist was not a chemist at all. We need only to turn to the Royal Society list of Bunsen's published researches, to see how many questions of a physical character were successfully solved by him. In his earlier days we have the Bunsen battery, with all the physical researches to which that gave rise: the Bunsen photometer with its wide application:

the long series of researches on gasometry to which I have alluded. Whilst in later years, first in importance comes the great discovery of spectrum analysis, with which the names of Bunsen and Kirchhoff will for ever be associated. Secondly may be mentioned the long series of researches of a difficult and complicated nature on the measurement of the chemical action of light, which he carried on in connexion with H. E. Roscoe. Next came the well-known invention of the burner, which could not have been accomplished had it not been for Bunsen's knowledge of the combustion phenomena of gases, arrived at by his previous investigations. Of his other work on physical chemistry it may suffice here to mention two examples, that of the ice- and of the vapour-calorimeter, in each of which Bunsen's wonderful power of exact experimentation and accurate workmanship is seen at its best.

Although Bunsen was in no sense a professed mathematician, and although some of the mathematical methods which he employed might perhaps be found fault with by a severe critic, yet he was able to apply mathematical treatment to chemical problems with success, and he was never weary of insisting upon the necessity of a knowledge of mathematics for all who desired to take up the study of chemistry.

His devotion to his pupils and to science brought round him, both at Marburg and later on at Heidelberg, a host of ardent workers, and enabled him to form a School of Chemistry at the latter University which, both as regards the quantity and certainly as regards the quality and far-reaching character of the work done by the master and his pupils, must be ranked at least as high as the older school of Liebig at Giessen. But not merely from his high scientific abilities is the name of Bunsen honoured by all those who have enjoyed the benefit of his acquaintance and friendship, but because they also found in him a man whom they could respect and admire.

Bunsen was elected an Honorary Fellow of the Physical Society of London on the 9th February, 1889.

JAMES LIVSEY HOWARD, D.Sc. (Lond.).—Dr. Howard was born at Rochdale on November 4th, 1866, and was educated at Manchester Grammar School. On leaving school in June 1883, he proceeded to study at University College, Liverpool, for a science degree in the London University. In July 1884 he passed the Intermediate Examination in Science, taking first-class honours in each of the three subjects: Mathematics, Chemistry, and Physics; being awarded in the latter subject the Neil Arnott Exhibition and Medal. In the following year he graduated B.Sc. with first-class honours in the same three subjects, taking the University Scholarship in Chemistry. In 1887 he obtained the degree of Doctor of Science. He then went to Heidelberg partly to study Physics under Professor Quincke, and likewise to gain an acquaintance with the German laboratories, methods of teaching, and language. After this he devoted a term to the study of Technical Electricity under Professor Ayrton at the City and Guilds of London Central Institution.

In October 1888 he was appointed by Professor Lodge Demonstrator of Physics in University College, Liverpool; subsequently also Lecturer on Physiography; and his interest was largely devoted to Liverpool ever since he began to study there. He frequently lectured for the Corporation to large audiences of artisans; and in his conduct of practical class was highly appreciated by the students for his zeal, industry, and patience.

He was for several years a Secretary of Section A of the British Association; and the Reports of those meetings published in 'The Times' newspaper were furnished by him each year since 1888.

A fair knowledge of French, German, and Italian enabled him to undertake translations of papers written in these languages; and he was on the staff of Abstractors for the Physical Society.

He has also written for various scientific journals, and frequently reviewed new books for them, especially for the 'Philosophical Magazine,' over the initials J. L. H.

His chief original papers were one in Wiedemann's *Annalen*, in conjunction with Professor Lenard, on the "Change of Resistance of Bismuth in a Magnetic Field," and one in the 'Philosophical Magazine,' in conjunction with Professor Lodge, on the "Concentration of Hertz Waves by Pitch Lenses"; but his College work did not leave him much time for original research, nor perhaps did his chief strength lie in that direction. His was the strength of great learning and of industrious and systematic labour, which might have been of the greatest benefit to science, had his life been prolonged.

He died on Sunday, November 26th, 1899, after six weeks' illness, at the age of 33.

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